

Form PTO-1390US DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE  
(Rev. 5-93)ATTORNEY'S DOCKET NO **H 4020 PCT/US****TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371**

U.S. APPLICATION NO. (if known sec 17 CFR 1.5)

**10/048208**INTERNATIONAL APPLICATION NO.  
**PCT/EP00/07163**INTERNATIONAL FILING DATE  
**August 2, 2000**PRIORITY DATE CLAIMED  
**August 5, 1999**

## TITLE OF INVENTION

**AGENT FOR DYING KERATIN FIBERS**

## APPLICANT(S) FOR DO/EO/US

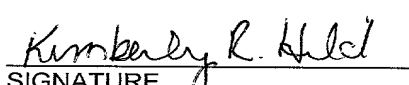
**Hinrich Moeller, Doris Oberkobusch, and Horst Hoeffkes,**

Applicant herewith submits to the United States Designated/Elected Office (EO/DO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
  2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
  3. ☐ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39 (1).
  4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
  5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2)).
    - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
    - b. ☒ has been transmitted by the International Bureau.
    - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
  6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
  7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
    - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
    - b. ☐ have been transmitted by the International Bureau.
    - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
    - d. ☒ have not been made and will not be made.
  8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
  9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). **UNEXECUTED**
  10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).
- Items 11. to 16. below concern other document(s) or information included:**
11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
  12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
  13. ☒ A **FIRST** preliminary amendment  
☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
  14. ☐ A substitute specification.
  15. ☐ A change of power of attorney and/or address letter.
  16. ☒ Other items or information.:

Version with Markings to Show Changes Made;  
 Information Disclosure Citation (Form PTO-1449) and References; and  
 International Search Report

"Express Mail" mailing label number **EL615774989US**

U.S. Application No. (If known see CFR 1.30) <b>10/048208</b>		INTERNATIONAL APPLICATION NO. <b>PCT/EP00/07163</b>		ATTORNEY'S DOCKET NUMBER <b>H 4020 PCT/US</b>	
17. ■ The following fees are submitted: <b>Basic National Fee (37 CFR 1.492(a)(1)-(5)):</b> Search Report has been prepared by the EPO or JPO..... <b>\$890.00</b>  International preliminary examination fee paid to USPTO (37CFR 1.482) ..... <b>\$710.00</b>  No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37CFR 1.445(a)(2)).... <b>\$740.00</b>  Neither international preliminary examination fee (37CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO. <b>\$1,040.00</b>  International preliminary examination fee paid to USPTO (37CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4)..... <b>\$100.00</b>  <b>ENTER APPROPRIATE BASIC FEE AMOUNT</b> =				CALCULATIONS      PTO USE ONLY	
				\$ 890      00 Order No. 02-0052	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date 37 (CFR 1.492(e)).				\$	
Claims	Number filed	Number Extra	Rate		
Total Claims	21- 20 =1	1	X 18.00	\$ 18 Order No. 02-0066	
Independent Claims	2- 3 =1	0	X 84.00	\$ 00	
Multiple dependent claims (s)(if applicable)			0	+ 280.00	\$ 00
<b>TOTAL OF ABOVE CALCULATIONS .....</b>				<b>=</b>	\$ 908
Reduction by ½ for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				\$	
<b>SUBTOTAL</b>				<b>=</b>	\$ 00
Processing fee of <b>\$130.00</b> for furnishing the English translation later the <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37CFR 1.492(f)).....				<b>+</b>	
<b>TOTAL NATIONAL FEE</b>				<b>=</b>	\$ 00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$	
<b>TOTAL FEES ENCLOSED</b>				<b>=</b>	\$ 908
				Amount to be: refunded	\$-----
				charged	
a. <input type="checkbox"/> A check in the amount of \$ _____ to cover the above fees is enclosed. b. ■ Please charge my Deposit Account No. <u>01-1250</u> in the amount of <b>\$ 890.00</b> to cover the above fees. A triplicate copy of this sheet is enclosed. Order No. _____ c. ■ The Assistant Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>01-1250</u> . A triplicate copy of this sheet is enclosed. <b>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must          be filed and granted to restore the application to pending status.</b>					
SEND ALL CORRESPONDENCE TO: Henkel Corporation, Law Dept. 2500 Renaissance Blvd., Ste. 200 Gulph Mills, PA 19406.....				 SIGNATURE	
				Kimberly R. Hild NAME ATTORNEY FOR APPLICANT 39,224 REGISTRATION NUMBER	

PATENT  
Docket No. H 4020 PCT/US

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

**In re Application of:**  
Moeller, et al.

**International Application No.** PCT/EP00/07163  
**International Filing Date:** August 2, 2000

**Serial No.** To be assigned **Examiner:** To be assigned

**Filed:** To be assigned **Art Unit:** To be assigned

**Title:** AGENT FOR DYING KERATIN FIBERS

"Express Mail Post Office to Addressee" service mailing label number EL 615774989 US

**PRELIMINARY AMENDMENT**

Box PCT  
Assistant Commissioner for Patents  
Washington, DC 20231

Attn: DO/EO/US

Sir:

Prior to examining this application, please amend the application as follows:

**In the Specification (Using the English Translation):**

On page 1 of the English translation, on a separate line between the title and line 1, please insert the following paragraph:

20040501 80284001

**Docket No. H4020 PCT/US  
PCT/EP00/07163**

**-- CROSS REFERENCE TO RELATED APPLICATIONS**

This application is a national stage application under 35 U.S.C. §371 of international application PCT/EP00/07163 filed on August 2, 2000, the international application not being published in English. This application also claims priority under 35 U.S.C. §119 to DE 199 36 911.9 filed on August 5, 1999. --

On page 1, on a separate line after the above inserted paragraph and before line 1, please insert the following header:

**-- BACKGROUND OF THE INVENTION -- .**

On page 3, on a separate line between lines 11 and 12, please insert the following header:

**--SUMMARY OF THE INVENTION--.**

On page 5, on a separate line between lines 17 and 18, please insert the following header:

**-- DETAILED DESCRIPTION OF THE INVENTION --.**

On page 27, line 1, please delete the heading "CLAIMS" and insert therefor:

**-- What is claimed is: --**

On a separate page, after page 36, please insert the enclosed Abstract of the Disclosure.

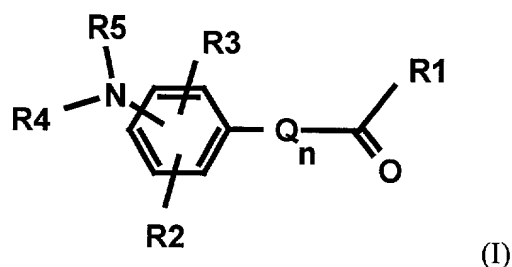
**In the Claims**

Please cancel Claims 1 to 13, without prejudice.

Please add the following new claims:

-- 14. (NEW) A composition for coloring keratin-containing fibers comprising a mixture of, or a reaction product of, or both of:

(A) at least one aromatic aldehyde or ketone corresponding to formula I:



wherein R<sup>1</sup> represents a hydrogen atom, a C<sub>1-4</sub> alkyl group or an aryl group,

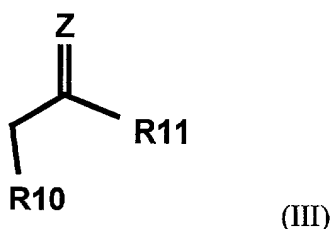
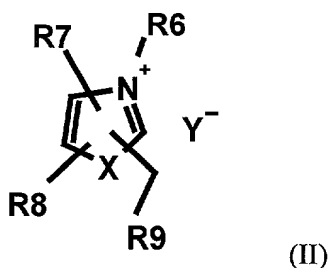
wherein R<sup>2</sup> and R<sup>3</sup>, independently of one another, represent a hydrogen atom, a C<sub>1-4</sub> alkyl group, a halogen atom, a hydroxy group, a C<sub>1-4</sub> alkoxy group or a nitro group, or R<sup>2</sup> and R<sup>3</sup> together form a fused aromatic ring,

wherein R<sup>4</sup> and R<sup>5</sup>, independently of one another, represent a hydrogen atom, a C<sub>1-4</sub> alkyl group, a C<sub>2-4</sub> hydroxyalkyl group, a C<sub>1-4</sub> alkenyl group or aryl group, or R<sup>4</sup> and R<sup>5</sup> together with the nitrogen atom form a five- to seven-membered heterocyclic ring, or one of R<sup>4</sup> or R<sup>5</sup> forms a saturated or unsaturated 5-, 6- or 7-membered ring with one of the substituents R<sup>2</sup> or R<sup>3</sup>,

wherein Q is a direct bond, a vinylene group or vinylidene group, wherein the vinylene group or vinylidene group may optionally together with one of the two substituents R<sup>4</sup> or R<sup>5</sup>, form an indole ring or an indoline ring, and

wherein n is 1 or 2; and

(B) one or more CH-active compounds corresponding to formula II, formula III, or mixtures thereof:



wherein R<sup>6</sup> represents a C<sub>1-10</sub> alkyl group, a C<sub>2-10</sub> alkenyl group, a C<sub>2-4</sub> hydroxyalkyl group, a C<sub>2-4</sub> carboxyalkyl group, a C<sub>2-4</sub> sulfoalkyl group or an aralkyl group,

wherein R<sup>7</sup> and R<sup>8</sup>, independently of one another, represent a hydrogen atom, a C<sub>1-4</sub> alkyl group, a halogen atom, a hydroxy group, a C<sub>1-4</sub> alkoxy group or a nitro group, or R<sup>7</sup> and R<sup>8</sup> together form a fused aromatic ring,

wherein R<sup>9</sup> represents a hydrogen atom, a C<sub>1-4</sub> alkyl group or an aryl group,

wherein X is an oxygen atom or sulfur atom, a >N-R<sup>12</sup> group or -CH=CH- group, where R<sup>12</sup> is a C<sub>1-4</sub> alkyl group, a C<sub>2-4</sub> carboxyalkyl group, a C<sub>2-4</sub> sulfoalkyl group, a C<sub>2-4</sub> sulfoxyalkyl group, a C<sub>2-4</sub> hydroxyalkyl group or an aralkyl group,

wherein Y<sup>-</sup> represents an anion selected from a halide, a C<sub>1-4</sub> alkyl sulfate, a C<sub>1-4</sub> alkane sulfonate, an arene sulfonate, a C<sub>1-4</sub> perfluoroalkanesulfonate, a tetrafluoroborate, a perhalogenate, a sulfate, a hydrogen sulfate or a carboxylate,

wherein R<sup>10</sup> represents a C<sub>1-4</sub> acyl group, an aroyl group, a C<sub>1-4</sub> alkylsulfonyl group, a C<sub>1-4</sub> alkylsulfinyl group, a C<sub>1-4</sub> alkylamino group, a di-C<sub>1-4</sub>-alkylamino group, a vinylcarbonyl group, a methineimino group, a nitrile group, an ester or a carboxylic acid amide group, the carboxylic acid amide group being optionally substituted by one or more C<sub>1-4</sub> alkyl, C<sub>2-4</sub> hydroxyalkyl or aryl groups,

wherein R<sup>11</sup> represents a C<sub>1-4</sub> acyl group, a C<sub>1-4</sub> alkoxy group, a C<sub>1-4</sub> alkylamino group, a C<sub>1-4</sub> acylamino group or a di-C<sub>1-4</sub>-alkylamino group, or wherein the substituents R<sup>10</sup> and R<sup>11</sup> together with the rest of the molecule form a 5-, 6- or 7-membered heterocycle selected from 1,3-thiazolidine-2,5-dione, 1,3-thiazolidine-2-thione-5-one, perhydropyrimidine-2,4,6-trione, perhydropyrimidine-2-thione-4,6-dione, cyclopentane-1,3-dione, cyclohexane-1,3-dione, indole, indan-1,3-dione, indan-1-one, 2-pyrazoline-5-one, 1,2-dihydro-6-hydroxy-2-hydroxypyridine or an enol ester derivative of the 5- to 7-membered heterocycle, and

wherein Z represents oxygen, sulfur or a dicyanomethylene group.

15. (NEW) The composition of claim 14 wherein the aromatic aldehyde or ketone of formula I comprises a compound selected from 4-dimethylaminobenzaldehyde, 4-diethylaminobenzaldehyde, 4-dimethylamino-2-hydroxybenzaldehyde, 4-pyrrolidinobenzaldehyde, 4-morpholinobenzaldehyde, 4-piperidinobenzaldehyde, 4-dimethylaminoacetophenone, 4-dimethylaminonaphthaldehyde, 4-dimethylaminobenzylidene acetone, 4-dimethylamino cinnamaldehyde, 2-dimethylaminobenzaldehyde, 2-chloro-4-dimethylaminobenzaldehyde, 4-dimethylamino-2-methylbenzaldehyde, trans-4-diethylaminocinnamaldehyde, 4-(dibutylamino)-benzaldehyde, 4-diphenylaminobenzaldehyde, 2,3,6,7-tetrahydro-1H,5H-benzo[ij]quinoxiline-9-carboxaldehyde, 4-dimethylamino-2-methoxybenzaldehyde, 2,3,6,7-tetrahydro-8-hydroxy-1H,5H-benzo[ij]quinoxiline-9-carboxaldehyde, 4-(1-imidazolyl)-benzaldehyde, 2-morpholinobenzaldehyde, indole-3-carboxaldehyde, 1-methylindole-3-carboxaldehyde, N-ethylcarbazole-3-aldehyde, 2-formylmethylene-1,3,3-trimethylindoline or mixtures thereof.

16. (NEW) The composition of claim 14, wherein the composition comprises a compound corresponding to formula II selected from a salt of 1,4-dimethylquinolinium, 1,2-dimethylquinolinium, 1,4-dimethylpyridinium, 1,2-dimethylpyridinium, 2-methyl-1-ethylquinolinium, 2,3-dimethylisoquinolinium, 1,2,3,3-tetramethyl-3H-indolinium, 2,3-dimethylbenzothiazolium, 2,3-dimethyl-6-nitrobenzothiazolium, 3-benzyl-2-benzothiazolium, 2-methyl-3-propyl benzothiazolium, 2,4-dimethyl-3-ethylthiazolium, 3-(2-carboxyethyl)-2.5-dimethylbenzothiazolium, 1,2,3-trimethylbenzimidazolium, 5,6-dichloro-1,3-diethyl-2-methyl benzimidazolium, 3-ethyl-2-methylbenzothiazolium, 3-ethyl-2-methylnaphtho[1,2-d]thiazolium, 5-chloro-3-ethyl-2-methylbenzothiazolium, or 3-ethyl-2-methyl benzoxazolium, or 2-methyl-3-(3-sulfopropyl)-benzothiazolium hydroxide or an inner salt thereof, or mixtures of any of the foregoing compounds corresponding to formula II.

17. (NEW) The composition of claim 16 wherein Y<sup>-</sup> of the salt comprises one or more chlorides, bromides, iodides, methanesulfonates, benzenesulfonates, p-toluenesulfonates, trifluoromethane sulfonates, methyl sulfates, tetrafluoroborates, or mixtures thereof.

18. (NEW) The composition of claim 14, wherein the composition comprises a compound corresponding to formula III selected from rhodanine, rhodanine-3-acetic acid, barbituric acid, thiobarbituric acid, 1,3-dimethyl thiobarbituric acid, 1,3-diethyl thiobarbituric acid, oxindole, 3-indoxyl acetate, coumaranone, 1-methyl-3-phenylpyrazolinone, indan-1,3-dione, cyclopentane-1,3-dione, 1,2-dihydro-1-ethyl-6-hydroxy-4-methyl-2-oxo-3-pyridinecarbonitrile or mixtures thereof.



19. (NEW) The composition of claim 14 wherein the composition comprises a reaction of the aromatic aldehyde or ketone of formula I and the CH-active compound, and the reaction product is selected from Quinaldine Red (2-[4-(dimethylamino)-styryl]-1-ethyl quinolinium iodide), 2-[4-(dimethylamino)-styryl]-1-methyl quinolinium iodide, 2-[4-(dimethylamino)-styryl]-1-ethylpyridinium iodide, 2-[4-(dimethylamino)-styryl]-1-methylpyridinium iodide, 4-[4-(dimethylaminostyryl)-1-methylpyridinium tosylate, 4-[2-(2,3,6,7-tetrahydro-1H,5H-benzo[*ij*]quinolizin-9-yl)-ethenyl]-1-methylpyridinium iodide, trans-4-[4-(dibutylamino)-styryl]-1-methyl pyridinium iodide, 2,6-bis-[4-(dimethylamino)-styryl]-1-methylpyridinium iodide, 2-[4-(dimethylamino)-styryl]-3-methyl benzoxazolium perchlorate, 2-[4-(dimethylamino)-styryl]-3-methyl benzoxazolium iodide, or 2-[4-(dimethylamino)-styryl]-1-ethylnaphthol[1,2-*d*]thiazolium iodide or mixtures thereof.

20. (NEW) The composition of claim 14, wherein the aromatic aldehyde or ketone corresponding to formula I and the compound of formula II or formula III are each present in the composition in an amount of 0.03 mmol to 65 mmol, based on 100 grams of the composition as a whole.

21. (NEW) The composition of claim 20, wherein the aromatic aldehyde or ketone corresponding to formula I and the compound of formula II or formula III are each present in the composition in an amount of 1 mmol to 40 mmol, based on 100 grams of the composition as a whole.

22. (NEW) The composition of claim 14, further comprising one or more color intensifiers selected from piperidine, piperidine-2-carboxylic acid, piperidine-3-carboxylic acid, piperidine-4-carboxylic acid, pyridine, 2-hydroxypyridine, 3-hydroxypyridine, 4-hydroxypyridine, imidazole, 1-methyl imidazole, histidine, pyrrolidine, proline, pyrrolidone, pyrrolidone-5-carboxylic acid, pyrazole, 1,2,4-triazole or piperazidine, or mixtures thereof.

23. (NEW) The composition of claim 14 further comprising from 0.01 weight percent to 20 weight percent, based on the total weight of the composition, of one or more substantive dyes selected from nitrophenylenediamines, nitroaminophenols, anthraquinones or indophenols, or combinations thereof.

24. (NEW) The composition of claim 14 further comprising one or more ammonium or metal salts selected from formates, carbonates, halides, sulfates, butyrates, valerates, caproates, acetates, lactates, glycolates, tartrates, citrates, gluconates, propionates, phosphates or phosphonates or combinations thereof.

25. (NEW) The composition of claim 24 wherein the cationic component of the ammonium or metal salts comprises one or more ammonium ions, alkali metals, alkaline earth metals, aluminum, manganese, iron, cobalt, copper or zinc or mixtures thereof.

26. (NEW) The composition of claim 14 further comprising one or more oxidizing agents.

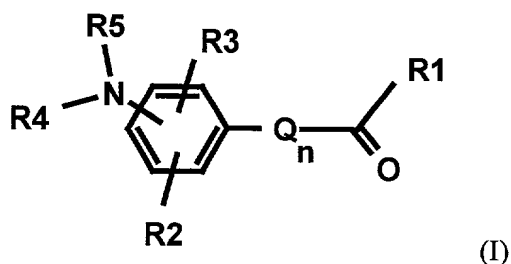
27. (NEW) The composition of claim 26 wherein the oxidizing agents comprise from 0.01 weight percent to 6 weight percent  $H_2O_2$ , based on the total weight of the composition.

28. (NEW) The composition of claim 14, further comprising one or more anionic, zwitterionic or nonionic surfactants, or combinations thereof.

29. (NEW) A method for coloring keratin-containing fibers comprising applying the composition of claim 14 to keratin-containing fibers.

30. (NEW) A process for coloring keratin-containing fibers comprising applying to keratin containing fibers

(a) at least one aromatic aldehyde or ketone corresponding to formula I:



wherein R<sup>1</sup> represents a hydrogen atom, a C<sub>1-4</sub> alkyl group or an aryl group,

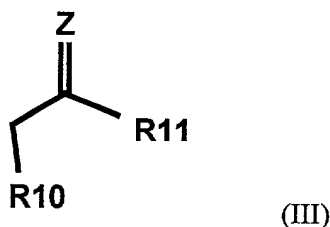
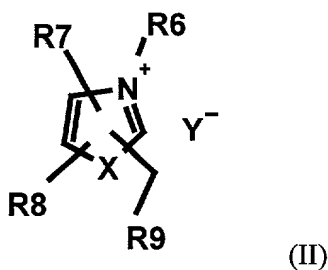
wherein R<sup>2</sup> and R<sup>3</sup>, independently of one another, represent a hydrogen atom, a C<sub>1-4</sub> alkyl group, a halogen atom, a hydroxy group, a C<sub>1-4</sub> alkoxy group or a nitro group, or R<sup>2</sup> and R<sup>3</sup> together form a fused aromatic ring,

wherein R<sup>4</sup> and R<sup>5</sup>, independently of one another, represent a hydrogen atom, a C<sub>1-4</sub> alkyl group, a C<sub>2-4</sub> hydroxyalkyl group, a C<sub>1-4</sub> alkenyl group or aryl group, or R<sup>4</sup> and R<sup>5</sup> together with the nitrogen atom form a five- to seven-membered heterocyclic ring, or one of R<sup>4</sup> or R<sup>5</sup> forms a saturated or unsaturated 5-, 6- or 7-membered ring with one of the substituents R<sup>2</sup> or R<sup>3</sup>,

wherein Q is a direct bond, a vinylene group or vinylidene group, wherein the vinylene group or vinylidene group may optionally together with one of the two substituents R<sup>4</sup> or R<sup>5</sup>, form an indole ring or an indoline ring, and

wherein n is 1 or 2; and

(b) one or more CH-active compounds corresponding to formula II, formula III or mixtures thereof:



wherein R<sup>6</sup> represents a C<sub>1-10</sub> alkyl group, a C<sub>2-10</sub> alkenyl group, a C<sub>2-4</sub> hydroxyalkyl group, a C<sub>2-4</sub> carboxyalkyl group, a C<sub>2-4</sub> sulfoalkyl group or an aralkyl group,

wherein R<sup>7</sup> and R<sup>8</sup>, independently of one another, represent a hydrogen atom, a C<sub>1-4</sub> alkyl group, a halogen atom, a hydroxy group, a C<sub>1-4</sub> alkoxy group or a nitro group, or R<sup>7</sup> and R<sup>8</sup> together form a fused aromatic ring,

wherein R<sup>9</sup> represents a hydrogen atom, a C<sub>1-4</sub> alkyl group or an aryl group,

wherein X is an oxygen atom or sulfur atom, a >N-R<sup>12</sup> group or -CH=CH- group, where R<sup>12</sup> is a C<sub>1-4</sub> alkyl group, a C<sub>2-4</sub> carboxyalkyl group, a C<sub>2-4</sub> sulfoalkyl group, a C<sub>2-4</sub> sulfoxyalkyl group, a C<sub>2-4</sub> hydroxyalkyl group or an aralkyl group,

wherein Y<sup>-</sup> represents an anion selected from a halide, a C<sub>1-4</sub> alkyl sulfate, a C<sub>1-4</sub> alkane sulfonate, an arene sulfonate, a C<sub>1-4</sub> perfluoroalkanesulfonate, a tetrafluoroborate, a perhalogenate, a sulfate, a hydrogen sulfate or a carboxylate,

wherein R<sup>10</sup> represents a C<sub>1-4</sub> acyl group, an aroyl group, a C<sub>1-4</sub> alkylsulfonyl group, a C<sub>1-4</sub> alkylsulfinyl group, a C<sub>1-4</sub> alkylamino group, a di-C<sub>1-4</sub>-alkylamino group, a vinylcarbonyl group, a methineimino group, a nitrile group, an ester or a carboxylic acid amide group, the carboxylic acid amide group being optionally substituted by one or more C<sub>1-4</sub> alkyl, C<sub>2-4</sub> hydroxyalkyl or aryl groups,

wherein R<sup>11</sup> represents a C<sub>1-4</sub> acyl group, a C<sub>1-4</sub> alkoxy group, a C<sub>1-4</sub> alkylamino group, a C<sub>1-4</sub> acylamino group or a di-C<sub>1-4</sub>-alkylamino group, or wherein the substituents R<sup>10</sup> and R<sup>11</sup> together with the rest of the molecule form a 5-, 6- or 7-membered heterocycle selected from 1,3-thiazolidine-2,5-dione, 1,3-thiazolidine-2-thione-5-one, perhydropyrimidine-2,4,6-trione, perhydropyrimidine-2-thione-4,6-dione, cyclopentane-1,3-dione, cyclohexane-1,3-dione, indole, indan-1,3-dione, indan-1-one, 2-pyrazoline-5-one, 1,2-dihydro-6-hydroxy-2-hydroxypyridine or an enol ester derivative of the 5- to 7-membered heterocycle, and

wherein Z represents oxygen, sulfur or a dicyanomethylene group.

31. (NEW) The method of claim 30 wherein the aromatic aldehyde or ketone of formula I and the CH-active compound are applied simultaneously or successively in any order to the keratin-containing fibers.

32. (NEW) The method of claim 30 wherein the aromatic aldehyde or ketone and the CH-active compound are formulated into a coloring composition prior to the applying step.

33. (NEW) The method of claim 32 wherein the coloring composition comprises a reaction product of the aromatic aldehyde or ketone and the CH-active compound.

34. (NEW) The method of claim 30 wherein the keratin-containing fiber is hair, and following the applying step, the aromatic aldehyde or ketone and the CH-active compound are washed out with a shampoo or rinsed out from the hair after a contact time of about 30 minutes. --

## REMARKS

Applicants respectfully request the Examiner to enter the above amendments prior to examination of this application.

## Status of Claims

Claims 14 to 34 will be pending after entry of the present amendment. Claims 1 to 13 are being canceled without prejudice.

### Amendment

The specification is being amended to insert section headers and an abstract of the disclosure in accordance with 37 CFR §1.77 to better conform with US patent practice. The specification is also being amended to insert a cross-reference to related applications in accordance 37 CFR §1.78 and to claim priority to those applications listed therein.

Attached hereto is a marked up version of the changes made to the specification entitled “Version With Markings To Show Changes Made.”

New Claims 14 to 34 replace original claims 1 to 13, and are being presented to better conform with US patent practice. These new claims are supported by the specification for example as shown in the Table below (cites to the specification are for the English translation):

Claim	Support in Specification
14	page 3, line 12 to page 5, line 17
15	page 5, line 26 to page 6, line 10
16, 17	page 6, lines 11 to 26
18	page 6, line 27 to page 7, line 2
19	page 7, lines 3 to 14
20, 21	page 7, lines 17 to 22
22	page 7, line 26 to page 8, line 3
23	page 8, line 17 to page 9, line 3
24, 25	page 16, lines 11 to 22
26, 27	page 8, lines 10 to 16
28	page 9, lines 24 to 30

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PCT/EP00/07163

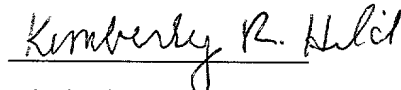
Claim	Support in Specification
29, 30, 31, 34	page 16, line 25 to page 21, line 19
32, 33	page 21, lines 20 to 27, page 22, lines 1 to 16

No new matter is added by the new claims or amendments to the specification.

**CONCLUSION**

Applicants respectfully request early and favorable notification of allowance of all pending claims. The Assistant Commissioner is authorized to charge any deficiency in the required fee or to credit any overpayment to Deposit Account 01-1250 in connection with this amendment.

Respectfully submitted,



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**Abstract of the Disclosure**

A coloring composition and a method of coloring keratin-containing fibers are provided. The coloring composition contains a mixture of and/or a reaction product of at least one aromatic aldehyde or ketone and at least one CH-active compound. In the method of the present invention, the aromatic aldehyde or ketone and the CH-active compound may be applied to keratin-containing fibers simultaneously or successively.

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## Agent for Dying Keratin Fibers

This invention relates to a composition for coloring keratin fibers, more particularly human hair, which contains a combination of aromatic aldehydes or ketones and CH-active compounds, to the use of this combination as a coloring component in hair colorants and to a process for coloring keratin-containing fibers, more particularly human hair.

In general, keratin-containing fibers, for example hair, wool or pelts, are dyed either with substantive dyes or with oxidation dyes which are formed by oxidative coupling of one or more primary intermediates with one another or with one or more secondary intermediates. Primary and secondary intermediates are also known as oxidation dye precursors.

The primary intermediates normally used are primary aromatic amines containing another free or substituted hydroxy or amino group in the para or ortho position, diaminopyridine derivatives, heterocyclic hydrazones, 4-aminopyrazolone derivatives and 2,4,5,6-tetraaminopyrimidine and derivatives thereof.

Special representatives are, for example, p-phenylenediamine, p-toluylenediamine, 2,4,5,6-tetraaminopyrimidine, p-aminophenol, N,N-bis-(2-hydroxyethyl)-p-phenylenediamine, 2-(2,5-diaminophenyl)-ethanol, 2-(2,5-diaminophenoxy)-ethanol, 1-phenyl-3-carboxyamido-4-amino-5-pyrazolone, 4-amino-3-methylphenol, 2-aminomethyl-4-aminophenol, 2-hydroxymethyl-4-aminophenol, 2-hydroxy-4,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine and 2,5,6-triamino-4-hydroxypyrimidine.

The secondary intermediates used are generally m-phenylenediamine derivatives, naphthols, resorcinol and resorcinol derivatives, pyrazolones, m-aminophenols and substituted pyridine derivatives. Particularly suitable secondary intermediates are  $\alpha$ -naphthol, 1,5-, 2,7- and 1,7-dihydroxynaphthalene, 5-amino-2-methylphenol, m-aminophenol,

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resorcinol, resorcinol monomethyl ether, m-phenylenediamine, 2,4-diaminophenoxyethanol, 2-amino-4-(2-hydroxyethylamino)-anisole (Lehmann's blue), 1-phenyl-3-methyl-5-pyrazolone, 2,4-dichloro-3-aminophenol, 1,3-bis-(2,4-diaminophenoxy)-propane, 2-chlororesorcinol, 4-chlororesorcinol, 2-chloro-6-methyl-3-aminophenol, 2-methyl resorcinol, 5-methyl resorcinol, 3-amino-6-methoxy-2-methylaminopyridine and 3,5-diamino-2,6-dimethoxypyridine.

With regard to other typical dye components, reference is specifically made to the series entitled "**Dermatology**" (Editors: Ch. Culnan and H. Maibach), Marcel Dekker Inc., New York/Basel, 1986, Vol. 7, Ch. Zviak, **The Science of Hair Care**, Chapter 7 (pages 248-250; Substantive Dyes) and Chapter 8 (pages 264-267; Oxidation Dye Precursors) and to the "**Europäische Inventar der Kosmetik-Rohstoffe**" published by the European Commission and available on floppy disk from the Bundesverband Deutscher Industrie- und Handelsunternehmen für Arzneimittel, Reformwaren und Körperpflegemittel e.V., Mannheim, Germany.

Although intensive colors with good fastness properties can be obtained with oxidation dyes, the color is generally developed under the influence of oxidizing agents, such as  $H_2O_2$  for example, which in some cases can result in damage to the fibers. In addition, some oxidation dye precursors or certain mixtures of oxidation dye precursors can occasionally have a sensitizing effect in people with sensitive skin. Although substantive dyes are applied under more moderate conditions, their disadvantage is that, in many cases, the colors obtained often have inadequate fastness properties.

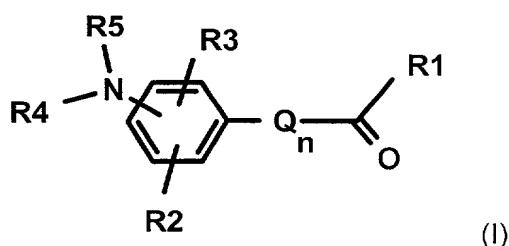
The use of the combination of aromatic aldehydes or ketones and CH-active compounds described hereinafter for coloring keratin-containing fibers has not hitherto been known.

The problem addressed by the present invention was to provide colorants for keratin fibers, more especially human hair, which would be at

least equivalent in quality to conventional oxidation hair dyes in regard to depth of color, grey coverage and fastness properties, but which would not necessarily have to contain oxidizing agents, such as  $H_2O_2$  for example. In addition, the colorants according to the invention would have very little, if any, sensitizing potential.

It has surprisingly been found that the combination of the aromatic aldehydes or ketones represented in formula I and CH-active compounds corresponding to formulae II and/or III is eminently suitable for coloring keratin-containing fibers, even in the absence of oxidizing agents. They give colors with excellent brilliance and depth of color and lead to a wide variety of shades. In principle, however, oxidizing agents may be present.

The present invention relates to a composition for coloring keratin-containing fibers, more particularly human hair, containing a combination of aromatic aldehydes or ketones corresponding to formula I:



in which

$R^1$  is a hydrogen atom, a  $C_{1-4}$  alkyl or an aryl group,

$R^2$  and  $R^3$  independently of one another represent a hydrogen atom, a  $C_{1-4}$  alkyl group, a halogen atom, a hydroxy,  $C_{1-4}$  alkoxy or nitro group or together form a fused aromatic ring,

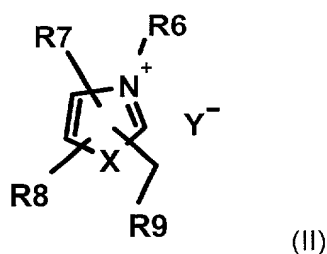
$R^4$  and  $R^5$  represent a hydrogen atom, a  $C_{1-4}$  alkyl,  $C_{2-4}$  hydroxyalkyl,  $C_{1-4}$  alkenyl or aryl group or, together with the nitrogen atom, form a five- to seven-membered heterocyclic ring or one of them forms a saturated or unsaturated 5-, 6- or 7-membered ring with one of the substituents  $R^2$  or

$R^3$ ,

Q is a direct bond or a vinylene or vinylidene group which, together with one of the two substituents  $R^4$  or  $R^5$ , may form an indole ring or - where an exocyclic double bond is formed - an indoline ring and

5  $n = 1$  or  $2$ ,

and CH-active compounds corresponding to formulae II and/or III:



10 in which

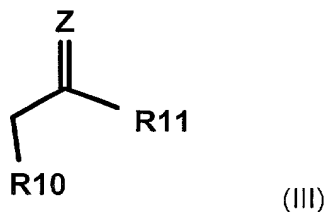
$R^6$  is a  $C_{1-10}$  alkyl,  $C_{2-10}$  alkenyl,  $C_{2-4}$  hydroxyalkyl,  $C_{2-4}$  carboxyalkyl,  $C_{2-4}$  sulfoalkyl or aralkyl group,

$R^7$  and  $R^8$  independently of one another represent a hydrogen atom, a  $C_{1-4}$  alkyl group, a halogen atom, a hydroxy,  $C_{1-4}$  alkoxy or nitro group or together form a fused aromatic ring,

15  $R^9$  represents a hydrogen atom, a  $C_{1-4}$  alkyl or an aryl group,

X is an oxygen or sulfur atom, the group  $>N-R^{12}$  or  $-CH=CH-$ , where  $R^{12}$  is a  $C_{1-4}$  alkyl,  $C_{2-4}$  carboxyalkyl,  $C_{2-4}$  sulfoalkyl,  $C_{2-4}$  sulfoxyalkyl,  $C_{2-4}$  hydroxyalkyl or aralkyl group, and

20  $Y^-$  is an anion selected from halide,  $C_{1-4}$  alkyl sulfate,  $C_{1-4}$  alkane sulfonate, arene sulfonate,  $C_{1-4}$  perfluoroalkanesulfonate, tetrafluoroborate, perhalogenate, sulfate, hydrogen sulfate or carboxylate,



in which

$R^{10}$  is a  $C_{1-4}$  acyl group, aroyl,  $C_{1-4}$  alkylsulfonyl,  $C_{1-4}$  alkylsulfinyl,  $C_{1-4}$  alkylamino, di- $C_{1-4}$ -alkylamino, vinylcarbonyl, methineimino, nitrile, ester or carboxylic acid amide group which may optionally be substituted by  $C_{1-4}$

5 alkyl,  $C_{2-4}$  hydroxyalkyl or aryl groups and

$R^{11}$  is a  $C_{1-4}$  acyl,  $C_{1-4}$  alkoxy,  $C_{1-4}$  alkylamino,  $C_{1-4}$  acylamino or di- $C_{1-4}$ -alkylamino group,

the substituents  $R^{10}$  and  $R^{11}$  together with the rest of the molecule forming  
a 5-, 6- or 7-membered heterocycle from the series of 1,3-thiazolidine-2,5-  
10 diones, 1,3-thiazolidine-2-thione-5-ones, perhydropyrimidine-2,4,6-triones,  
perhydropyrimidine-2-thione-4,6-diones, cyclopentane-1,3-diones, cyclo-  
hexane-1,3-diones, indolines, indan-1,3-diones, indan-1-ones, 2-  
pyrazoline-5-ones, 1,2-dihydro-6-hydroxy-2-hydroxypyridines or enol esters  
thereof, and

15 Z represents oxygen, sulfur or the dicyanomethylene group,

and/or reaction products of the compounds corresponding to formulae I  
and II and/or III.

In the context of the invention, keratin-containing fibers are  
understood to include wool, pelts, feathers and, in particular, human hair.

20 In principle, however, the colorants according to the invention may also be  
used to color other natural fibers such as, for example, cotton, jute, sisal,  
linen or silk, modified natural fibers such as, for example, regenerated  
cellulose, nitro, alkyl or hydroxyalkyl or acetyl cellulose and synthetic fibers  
such as, for example, polyamide, polyacrylonitrile, polyurethane and  
25 polyester fibers.

Preferred compounds corresponding to formula I are, for example,  
4-dimethylaminobenzaldehyde, 4-diethylaminobenzaldehyde, 4-dimethyl-  
amino-2-hydroxybenzaldehyde, 4-pyrrolidinobenzaldehyde, 4-morpholino-  
benzaldehyde, 4-piperidinobenzaldehyde, 4-dimethylaminoacetophenone,  
30 4-dimethylaminonaphthaldehyde, 4-dimethylaminobenzylidene acetone, 4-

dimethylamino cinnamaldehyde, 2-dimethylaminobenzaldehyde, 2-chloro-4-dimethylaminobenzaldehyde, 4-dimethylamino-2-methylbenzaldehyde, trans-4-diethylaminocinnamaldehyde, 4-(dibutylamino)-benzaldehyde, 4-diphenylaminobenzaldehyde, 2,3,6,7-tetrahydro-1H,5H-benzo[ij]quino-  
5 ziline-9-carboxaldehyde, 4-dimethylamino-2-methoxybenzaldehyde, 2,3,6,7-tetrahydro-8-hydroxy-1H,5H-benzo[ij]quinoxaline-9-carboxaldehyde, 4-(1-imidazolyl)-benzaldehyde, 2-morpholinobenzaldehyde, indole-3-carboxaldehyde, 1-methylindole-3-carboxaldehyde, N-ethylcarbazole-3-aldehyde, 2-formylmethylene-1,3,3-trimethylindoline (Fischer's aldehyde or  
10 tribase aldehyde) and mixtures thereof.

Examples of preferred compounds corresponding to formula II are 1,4-dimethylquinolinium, 1,2-dimethylquinolinium, 1,4-dimethylpyridinium, 1,2-dimethylpyridinium, 2-methyl-1-ethylquinolinium, 2,3-dimethylisoquinolinium, 1,2,3,3-tetramethyl-3H-indolinium, 2,3-  
15 dimethylbenzothiazolium, 2,3-dimethyl-6-nitrobenzothiazolium, 3-benzyl-2-benzothiazolium, 2-methyl-3-propyl benzothiazolium, 2,4-dimethyl-3-ethylthiazolium, 3-(2-carboxyethyl)-2,5-dimethylbenzothiazolium, 1,2,3-trimethylbenzimidazolium, 5,6-dichloro-1,3-diethyl-2-methyl  
benzimidazolium, 3-ethyl-2-methylbenzothiazolium, 3-ethyl-2-  
20 methylnaphtho[1,2-d]thiazolium, 5-chloro-3-ethyl-2-methylbenzothiazolium, 3-ethyl-2-methyl benzoxazolium salts which may be present, for example, as chlorides, bromides, iodides, methanesulfonates, benzenesulfonates, p-toluenesulfonates, trifluoromethane sulfonates, methyl sulfates, tetra-  
fluoroborates and 2-methyl-3-(3-sulfopropyl)-benzothiazolium hydroxide,  
25 inner salt, 5-methoxy-2-methyl-3-(3-sulfopropyl)-benzothiazolium hydroxide, inner salt and mixtures of the above.

Examples of compounds corresponding to formula III are rhodanine, rhodanine-3-acetic acid, barbituric acid, thiobarbituric acid, 1,3-dimethyl and 1,3-diethyl thiobarbituric acid, oxindole, 3-indoxyl acetate,  
30 coumaranone, 1-methyl-3-phenylpyrazolinone, indan-1,3-dione,

cyclopentane-1,3-dione, 1,2-dihydro-1-ethyl-6-hydroxy-4-methyl-2-oxo-3-pyridinecarbonitrile and mixtures of the above.

Examples of reaction products of the compounds corresponding to formulae I and II and/or III are Quinaldine Red (2-[4-(dimethylamino)-styryl]-1-ethyl quinolinium iodide), 2-[4-(dimethylamino)-styryl]-1-methyl quinolinium iodide, 2-[4-(dimethylamino)-styryl]-1-ethylpyridinium iodide, 2-[4-(dimethylamino)-styryl]-1-methylpyridinium iodide, 4-[4-(dimethylaminostyryl)-1-methyl pyridinium tosylate, 4-[2-(2,3,6,7-tetrahydro-1H,5H-benzo[ij]quinolizin-9-yl)-ethenyl]-1-methylpyridinium iodide, trans-4-[4-(dibutylamino)-styryl]-1-methyl pyridinium iodide and 2,6-bis-[4-(dimethylamino)-styryl]-1-methylpyridinium iodide, 2-[4-(dimethylamino)-styryl]-3-methyl benzoxazolium perchlorate, 2-[4-(dimethylamino)-styryl]-3-methyl benzoxazolium iodide, 2-[4-(dimethylamino)-styryl]-1-ethylnaphthol[1,2-d]thiazolium iodide.

These compounds are largely known from the literature or are commercially obtainable or may be obtained by known syntheses.

The above-mentioned compounds corresponding to formula I, formula II and formula III are used in the compositions according to the invention in quantities of preferably 0.03 to 65 mmol and more preferably 1 to 40 mmol, based on 100 g of the colorant as a whole. They may be used as substantive colorants or in the presence of typical oxidation dye precursors.

Colorants which contain the combination according to the invention as sole coloring component are preferably used for colors in the yellow, orange, red and violet range.

In order to obtain further and more intensive colors, the colorants according to the invention may additionally contain color intensifiers. The color intensifiers are preferably selected from the group consisting of piperidine, piperidine-2-carboxylic acid, piperidine-3-carboxylic acid, piperidine-4-carboxylic acid, pyridine, 2-hydroxypyridine, 3-hydroxypyridine,

4-hydroxypyridine, imidazole, 1-methyl imidazole, histidine, pyrrolidine, proline, pyrrolidone, pyrrolidone-5-carboxylic acid, pyrazole, 1,2,4-triazole, piperazine, derivatives and physiologically compatible salts thereof.

The color intensifiers mentioned above may be used in a quantity of  
5 0.03 to 65 and more particularly 1 to 40 mmol, based on 100 g of the colorant as a whole.

Various combinations of the compounds corresponding to formula I, II and/or III may also be used together in all colorants. Similarly, various color intensifiers may also be used together.

10 Oxidizing agents, for example  $H_2O_2$ , need not be present. However, it may be desirable in some cases to add hydrogen peroxide or other oxidizing agents to the compositions according to the invention to obtain shades which are lighter than the keratin-containing fibers to be colored. Oxidizing agents are generally used in a quantity of 0.01 to 6% by weight,  
15 based on the solution applied. A preferred oxidizing agent for human hair is  $H_2O_2$ .

In one preferred embodiment, the colorants according to the invention contain typical substantive dyes, for example from the group of nitrophenylenediamines, nitroaminophenols, anthraquinones or  
20 indophenols, in addition to the compounds present in accordance with the invention in order further to modify the color tones. Examples of suitable substantive dyes are the compounds known under the International names or commercial names of HC Yellow 2, HC Yellow 4, HC Yellow 6, Basic Yellow 57, Disperse Orange 3, HC Red 3, HC Red BN, Basic Red 76, HC  
25 Blue 2, Disperse Blue 3, Basic Blue 99, HC Violet 1, Disperse Violet 1, Disperse Violet 4, Disperse Black 9, Basic Brown 16 and Basic Brown 17 and also picramic acid, 2-amino-6-chloro-4-nitrophenol, 4-amino-2-nitrodiphenylamine-2'-carboxylic acid, 6-nitro-1,2,3,4-tetrahydroquinoxaline, 4-N-ethyl-1,4-bis-(2'-hydroxyethylamino)-2-nitrobenzene hydrochloride and  
30 1-methyl-3-nitro-4-(2'-hydroxyethyl)-aminobenzene. The compositions



according to the invention in this embodiment contain the substantive dyes in a quantity of, preferably, 0.01 to 20% by weight, based on the colorant as a whole.

In addition, the compositions according to the invention may also  
5 contain naturally occurring dyes such as, for example, henna red, henna neutral, henna black, camomile blossom, sandalwood, black tea, black alder bark, sage, logwood, madder root, catechu, sedre and alkanet.

Compounds I and II present in accordance with the invention or the color intensifiers and substantive dyes optionally present do not have to be  
10 single compounds. Instead, the hair colorants according to the invention - due to the processes used for producing the individual dyes - may contain small quantities of other components providing they do not adversely affect the coloring result or have to be ruled out for other reasons, for example toxicological reasons.

15 The colorants according to the invention produce intensive colors even at physiologically compatible temperatures of  $<45^{\circ}\text{C}$ . Accordingly, they are particularly suitable for coloring human hair. For application to human hair, the colorants are normally incorporated in a water-containing cosmetic carrier. Suitable water-containing cosmetic carriers are, for  
20 example, creams, emulsions, gels or even surfactant-containing foaming solutions, for example shampoos or other formulations suitable for application to the keratin-containing fibers. If necessary, the colorants may even be incorporated in water-free carriers.

The colorants according to the invention may also contain any of the  
25 known active substances, additives and auxiliaries typical of such formulations. In many cases, the colorants contain at least one surfactant, both anionic and zwitterionic, ampholytic, nonionic and cationic surfactants being suitable in principle. In many cases, however, it has been found to be of advantage to select the surfactants from anionic, zwitterionic or  
30 nonionic surfactants.

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- Suitable anionic surfactants for the compositions according to the invention are any anionic surface-active substances suitable for use on the human body. Such substances are characterized by a water-solubilizing anionic group such as, for example, a carboxylate, sulfate, sulfonate or phosphate group and a lipophilic alkyl group containing around 10 to 22 carbon atoms. In addition, glycol or polyglycol ether groups, ester, ether, amide groups and hydroxyl groups may also be present in the molecule. The following are examples of suitable anionic surfactants - in the form of the sodium, potassium and ammonium salts and the mono-, di- and trialkanolammonium salts containing 2 or 3 carbon atoms in the alkanol group:
- linear fatty acids containing 10 to 22 carbon atoms (soaps),
  - ether carboxylic acids corresponding to the formula  $R-O-(CH_2-CH_2O)_x-CH_2-COOH$ , in which R is a linear alkyl group containing 10 to 22 carbon atoms and  $x = 0$  or 1 to 16,
  - acyl sarcosides containing 10 to 18 carbon atoms in the acyl group,
  - acyl taurides containing 10 to 18 carbon atoms in the acyl group,
  - acyl isethionates containing 10 to 18 carbon atoms in the acyl group,
  - sulfosuccinic acid mono- and dialkyl esters containing 8 to 18 carbon atoms in the alkyl group and sulfosuccinic acid monoalkyl polyoxyethyl esters containing 8 to 18 carbon atoms in the alkyl group and 1 to 6 oxyethyl groups,
  - linear alkane sulfonates containing 12 to 18 carbon atoms,
  - linear  $\alpha$ -olefin sulfonates containing 12 to 18 carbon atoms,
  - $\alpha$ -sulfofatty acid methyl esters of fatty acids containing 12 to 18 carbon atoms,
  - alkyl sulfates and alkyl polyglycol ether sulfates corresponding to the formula  $R-O(CH_2-CH_2O)_x-SO_3H$ , in which R is a preferably linear alkyl group containing 10 to 18 carbon atoms and  $x = 0$  or 1 to 12,
  - mixtures of surface-active hydroxysulfonates according to **DE-A-37 25**

030,

- sulfated hydroxyalkyl polyethylene and/or hydroxyalkylene propylene glycol ethers according to **DE-A-37 23 354**,
- sulfonates of unsaturated fatty acids containing 12 to 24 carbon atoms and 1 to 6 double bonds according to **DE-A-39 26 344**,
- esters of tartaric acid and citric acid with alcohols in the form of addition products of around 2 to 15 molecules of ethylene oxide and/or propylene oxide with fatty alcohols containing 8 to 22 carbon atoms.

Preferred anionic surfactants are alkyl sulfates, alkyl polyglycol ether sulfates and ether carboxylic acids containing 10 to 18 carbon atoms in the alkyl group and up to 12 glycol ether groups in the molecule and, in particular, salts of saturated and, more particularly, unsaturated C<sub>8-22</sub> carboxylic acids, such as oleic acid, stearic acid, isostearic acid and palmitic acid.

In the context of the invention, zwitterionic surfactants are surface-active compounds which contain at least one quaternary ammonium group and at least one -COO<sup>(-)</sup> or -SO<sub>3</sub><sup>(-)</sup> group in the molecule. Particularly suitable zwitterionic surfactants are the so-called betaines, such as N-alkyl-N,N-dimethyl ammonium glycinate, for example coconutalkyl dimethyl ammonium glycinate, N-acylaminopropyl-N,N-dimethyl ammonium glycinate, for example coconutacylaminopropyl dimethyl ammonium glycinate, and 2-alkyl-3-carboxymethyl-3-hydroxyethyl imidazolines containing 8 to 18 carbon atoms in the alkyl or acyl group and coconutacylaminoethyl hydroxyethyl carboxymethyl glycinate. A preferred zwitterionic surfactant is the fatty acid amide derivative known by the CTFA name of Cocamidopropyl Betaine.

Ampholytic surfactants are surface-active compounds which, in addition to a C<sub>8-18</sub> alkyl or acyl group, contain at least one free amino group and at least one -COOH or -SO<sub>3</sub>H group in the molecule and which are capable of forming inner salts. Examples of suitable ampholytic surfactants

are N-alkyl glycines, N-alkyl propionic acids, N-alkyl aminobutyric acids, N-alkyl iminodipropionic acids, N-hydroxyethyl-N-alkyl amidopropyl glycines, N-alkyl taurines, N-alkyl sarcosines, 2-alkyl aminopropionic acids and alkyl aminoacetic acids containing around 8 to 18 carbon atoms in the alkyl group. Particularly preferred ampholytic surfactants are N-coconutalkyl aminopropionate, coconutacyl aminoethyl aminopropionate and C<sub>12-18</sub> acyl sarcosine.

Nonionic surfactants contain, for example, a polyol group, a polyalkylene glycol ether group or a combination of polyol and polyglycol ether groups as the hydrophilic group. Examples of such compounds are

- products of the addition of 2 to 30 moles of ethylene oxide and/or 0 to 5 moles of propylene oxide onto linear fatty alcohols containing 8 to 22 carbon atoms, onto fatty acids containing 12 to 22 carbon atoms and onto alkylphenols containing 8 to 15 carbon atoms in the alkyl group,
- C<sub>12-22</sub> fatty acid monoesters and diesters of products of the addition of 1 to 30 moles of ethylene oxide onto glycerol,
- C<sub>8-22</sub> alkyl mono- and oligoglycosides and ethoxylated analogs thereof,
- products of the addition of 5 to 60 moles of ethylene oxide onto castor oil and hydrogenated castor oil,
- products of the addition of ethylene oxide onto sorbitan fatty acid esters,
- products of the addition of ethylene oxide onto fatty acid alkanolamides.

Examples of cationic surfactants suitable for use in the hair treatment formulations according to the invention are, in particular, quaternary ammonium compounds. Preferred quaternary ammonium compounds are ammonium halides, such as alkyl trimethyl ammonium chlorides, dialkyl dimethyl ammonium chlorides and trialkyl methyl ammonium chlorides, for example cetyl trimethyl ammonium chloride, stearyl trimethyl ammonium chloride, distearyl dimethyl ammonium chloride, lauryl dimethyl ammonium chloride, lauryl dimethyl benzyl ammonium chloride and tricetyl methyl ammonium chloride. Other cationic

surfactants suitable for use in accordance with the invention are the quaternized protein hydrolyzates.

Also suitable for use in accordance with the invention are cationic silicone oils such as, for example, the commercially available products Q2-  
5 7224 (manufacturer: Dow Corning; a stabilized trimethyl silyl amodimethicone), Dow Corning 929 Emulsion (containing a hydroxylamino-modified silicone which is also known as amodimethicone), SM-2059 (manufacturer: General Electric), SLM-55067 (manufacturer: Wacker) and Abil®-Quat  
10 3270 and 3272 (manufacturer: Th. Goldschmidt; diquateryary polydimethyl siloxanes, quaternium-80).

Alkyl amidoamines, particularly fatty acid amidoamines, such as the stearyl amidopropyl dimethyl amine obtainable as Tego Amid®S 18, are distinguished not only by their favorable conditioning effect, but also and in particular by their ready biodegradability.

15 Quaternary ester compounds, so-called "esterquats", such as the methyl hydroxyalkyl dialkoyloxyalkyl ammonium methosulfates marketed under the trade name of Stepantex®, are also readily biodegradable.

One example of a quaternary sugar derivative suitable for use as a cationic surfactant is the commercially available product Glucquat®100  
20 (CTFA name: Lauryl Methyl Gluceth-10 Hydroxypropyl Dimonium Chloride).

The compounds containing alkyl groups used as surfactants may be single compounds. In general, however, these compounds are produced from native vegetable or animal raw materials so that mixtures with  
25 different alkyl chain lengths dependent upon the particular raw material are obtained.

The surfactants representing addition products of ethylene and/or propylene oxide with fatty alcohols or derivatives of these addition products may be both products with a "normal" homolog distribution and products  
30 with a narrow homolog distribution. Products with a "normal" homolog

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distribution are mixtures of homologs which are obtained in the reaction of fatty alcohol and alkylene oxide using alkali metals, alkali metal hydroxides or alkali metal alcoholates as catalysts. By contrast, narrow homolog distributions are obtained when, for example, hydrotalcites, alkaline earth metal salts of ether carboxylic acids, alkaline earth metal oxides, hydroxides or alcoholates are used as catalysts. The use of products with a narrow homolog distribution can be of advantage.

Other active substances, auxiliaries and additives are, for example,

- nonionic polymers such as, for example, vinyl pyrrolidone/vinyl acrylate copolymers, polyvinyl pyrrolidone and vinyl pyrrolidone/vinyl acetate copolymers and polysiloxanes,
- cationic polymers, such as quaternized cellulose ethers, polysiloxanes containing quaternary groups, dimethyl diallyl ammonium chloride polymers, acrylamide/dimethyl diallyl ammonium chloride copolymers, dimethyl aminoethyl methacrylate/vinyl pyrrolidone copolymers quaternized with diethyl sulfate, vinyl pyrrolidone/imidazolinium methochloride copolymers and quaternized polyvinyl alcohol,
- zwitterionic and amphoteric polymers such as, for example, acrylamido-propyl/trimethyl ammonium chloride/acrylate copolymers and octyl acrylamide/methyl methacrylate/tert.butyl aminoethyl methacrylate/2-hydroxypropyl methacrylate copolymers,
- anionic polymers such as, for example, polyacrylic acids, crosslinked polyacrylic acids, vinyl acetate/crotonic acid copolymers, vinyl pyrrolidone/vinyl acrylate copolymers, vinyl acetate/butyl maleate/isobornyl acrylate copolymers, methyl vinyl ether/maleic anhydride copolymers and acrylic acid/ethyl acrylate/N-tert.butyl acrylamide terpolymers,
- thickeners, such as agar agar, guar gum, alginates, xanthan gum, gum arabic, karaya gum, locust bean gum, linseed gums, dextrans, cellulose derivatives, for example methyl cellulose, hydroxyalkyl cellulose and

carboxymethyl cellulose, starch fractions and derivatives, such as amylose, amylopectin and dextrans, clays such as, for example, bentonite or fully synthetic hydrocolloids such as, for example, polyvinyl alcohol.

- 5 - structurants, such as glucose and maleic acid,  
- hair-conditioning compounds, such as phospholipids, for example soya lecithin, egg lecithin and kephalins, and also silicone oils,  
- protein hydrolyzates, more particularly elastin, collagen, keratin, milk protein, soya protein and wheat protein hydrolyzates, condensation  
10 products thereof with fatty acids and quaternized protein hydrolyzates,  
- perfume oils, dimethyl isosorbide and cyclodextrins,  
- solubilizers, such as ethanol, isopropanol, ethylene glycol, propylene glycol, glycerol and diethylene glycol,  
- antidandruff agents, such as Piroctone Olamine and Zinc Omadine,  
15 - other substances for adjusting the pH value,  
- active substances, such as panthenol, pantothenic acid, allantoin, pyrrolidone carboxylic acids and salts thereof, plant extracts and vitamins,  
- cholesterol,  
20 - UV filters,  
- consistency factors, such as sugar esters, polyol esters or polyol alkyl ethers,  
- fats and waxes, such as spermaceti, beeswax, montan wax, paraffins, fatty alcohols and fatty acid esters,  
25 - fatty acid alkanolamides,  
- complexing agents, such as EDTA, NTA and phosphonic acids,  
- swelling and penetration agents, such as glycerol, propylene glycol monoethyl ether, carbonates, hydrogen carbonates, guanidines, ureas and primary, secondary and tertiary phosphates, imidazoles, tannins,  
30 pyrrole,

- opacifiers, such as latex,
  - pearlizers, such as ethylene glycol mono- and distearate,
  - propellents, such as propane/butane mixtures, N<sub>2</sub>O, dimethyl ether, CO<sub>2</sub> and air and
- 5     - antioxidants.

To produce the colorants according to the invention, the constituents of the water-containing carrier are used in the usual quantities for this purpose. For example, emulsifiers are used in concentrations of 0.5 to 30% by weight while thickeners are used in concentrations of 0.1 to 25% by weight, based on the colorant as a whole.

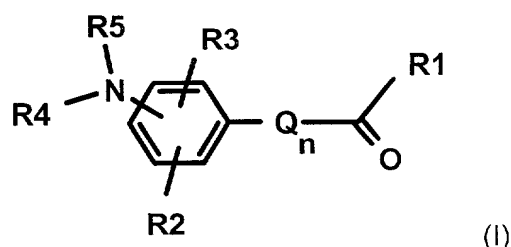
It can be of advantage to the coloring result to add ammonium or metal salts to the colorants. Suitable metal salts are, for example, formates, carbonates, halides, sulfates, butyrates, valerates, caproates, acetates, lactates, glycolates, tartrates, citrates, gluconates, propionates, phosphates and phosphonates of alkali metals, such as potassium, sodium or lithium, alkaline earth metals, such as magnesium, calcium, strontium or barium, or of aluminium, manganese, iron, cobalt, copper or zinc, sodium acetate, lithium bromide, calcium bromide, calcium gluconate, zinc chloride, zinc sulfate, magnesium chloride, magnesium sulfate, ammonium carbonate, chloride and acetate being preferred. These salts are preferably present in a quantity of 0.03 to 65 mmol and more preferably in a quantity of 1 to 40 mmol, based on 100 g of the colorant as a whole.

The pH value of the ready-to-use coloring compositions is normally in the range from 2 to 12 and preferably in the range from 4 to 10.

The present invention also relates to the use of a combination of aromatic aldehydes or ketones corresponding to formula I:

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in which

$R^1$  is a hydrogen atom, a  $C_{1-4}$  alkyl or an aryl group,

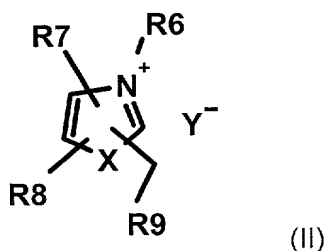
- 5  $R^2$  and  $R^3$  independently of one another represent a hydrogen atom, a  $C_{1-4}$  alkyl group, a halogen atom, a hydroxy,  $C_{1-4}$  alkoxy or nitro group or together form a fused aromatic ring,

- $R^4$  and  $R^5$  represent a hydrogen atom, a  $C_{1-4}$  alkyl,  $C_{2-4}$  hydroxyalkyl,  $C_{1-4}$  alkenyl or aryl group or, together with the nitrogen atom, form a five- to  
 10 seven-membered heterocyclic ring or one of them forms a saturated or unsaturated 5-, 6- or 7-membered ring with one of the substituents  $R^2$  or  $R^3$ ,

- $Q$  is a direct bond or a vinylene or vinylidene group which, together with one of the two substituents  $R^4$  or  $R^5$ , may form an indole ring or - where an  
 15 exocyclic double bond is formed - an indoline ring and

$n = 1$  or  $2$ ,

and CH-active compounds corresponding to formulae II and/or III:



20

in which

$R^6$  is a  $C_{1-10}$  alkyl,  $C_{2-10}$  alkenyl,  $C_{2-4}$  hydroxyalkyl,  $C_{2-4}$  carboxyalkyl,  $C_{2-4}$

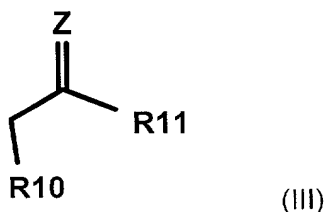
sulfoalkyl or aralkyl group,

$R^7$  and  $R^8$  independently of one another represent a hydrogen atom, a  $C_{1-4}$  alkyl group, a halogen atom, a hydroxy,  $C_{1-4}$  alkoxy or nitro group or together form a fused aromatic ring,

5  $R^9$  represents a hydrogen atom, a  $C_{1-4}$  alkyl or an aryl group,

X is an oxygen or sulfur atom, the group  $>N-R^{12}$  or  $-CH=CH-$ , where  $R^{12}$  is a  $C_{1-4}$  alkyl,  $C_{2-4}$  carboxyalkyl,  $C_{2-4}$  sulfoalkyl,  $C_{2-4}$  sulfoxyalkyl,  $C_{2-4}$  hydroxyalkyl or aralkyl group, and

10  $Y^-$  is an anion selected from halide,  $C_{1-4}$  alkyl sulfate,  $C_{1-4}$  alkane sulfonate, arene sulfonate,  $C_{1-4}$  perfluoroalkanesulfonate, tetrafluoroborate, perhalogenate, sulfate, hydrogen sulfate or carboxylate,



in which

15  $R^{10}$  is a  $C_{1-4}$  acyl group, aroyl,  $C_{1-4}$  alkylsulfonyl,  $C_{1-4}$  alkylsulfinyl,  $C_{1-4}$  alkylamino, di- $C_{1-4}$ -alkylamino, vinylcarbonyl, methineimino, nitrile, ester or carboxylic acid amide group which may optionally be substituted by  $C_{1-4}$  alkyl,  $C_{2-4}$  hydroxyalkyl or aryl groups and

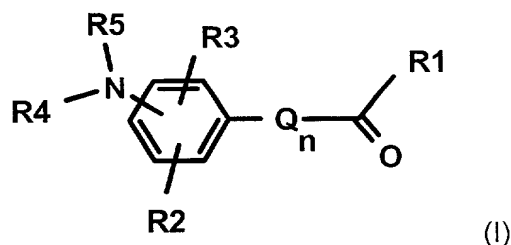
$R^{11}$  is a  $C_{1-4}$  acyl,  $C_{1-4}$  alkoxy,  $C_{1-4}$  alkylamino,  $C_{1-4}$  acylamino or di- $C_{1-4}$ -alkylamino group,

20 the substituents  $R^{10}$  and  $R^{11}$  together with the rest of the molecule forming a 5-, 6- or 7-membered heterocycle from the series of 1,3-thiazolidine-2,5-diones, 1,3-thiazolidine-2-thione-5-ones, perhydropyrimidine-2,4,6-triones, perhydropyrimidine-2-thione-4,6-diones, cyclopentane-1,3-diones, cyclohexane-1,3-diones, indolines, indan-1,3-diones, indan-1-ones, 2-  
25 pyrazoline-5-ones, 1,2-dihydro-6-hydroxy-2-hydroxypyridines or enol esters thereof, and

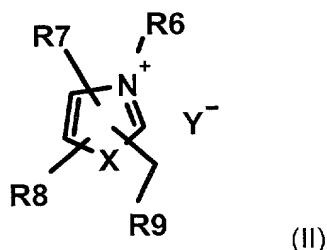
Z represents oxygen, sulfur or the dicyanomethylene group,

and/or reaction products of these compounds,  
as a coloring component in oxidation hair colorants.

The present invention also relates to a process for coloring keratin-containing fibers, more particularly human hair, in which a colorant  
5 containing a combination of aromatic aldehyde or ketones corresponding to formula I:



- 10 in which  
 $R^1$  is a hydrogen atom, a  $C_{1-4}$  alkyl or an aryl group,  
 $R^2$  and  $R^3$  independently of one another represent a hydrogen atom, a  $C_{1-4}$   
alkyl group, a halogen atom, a hydroxy,  $C_{1-4}$  alkoxy or nitro group or  
together form a fused aromatic ring,  
15  $R^4$  and  $R^5$  represent a hydrogen atom, a  $C_{1-4}$  alkyl,  $C_{2-4}$  hydroxyalkyl,  $C_{1-4}$   
alkenyl or aryl group or, together with the nitrogen atom, form a five- to  
seven-membered heterocyclic ring or one of them forms a saturated or  
unsaturated 5-, 6- or 7-membered ring with one of the substituents  $R^2$  or  
 $R^3$ ,  
20 Q is a direct bond or a vinylene or vinylidene group which, together with  
one of the two substituents  $R^4$  or  $R^5$ , may form an indole ring or - where an  
exocyclic double bond is formed - an indoline ring and  
n = 1 or 2,  
and CH-active compounds corresponding to formulae II and/or III:



in which

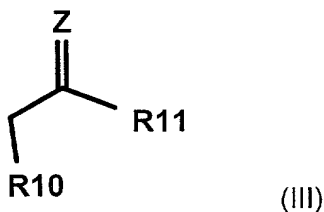
$R^6$  is a  $C_{1-10}$  alkyl,  $C_{2-10}$  alkenyl,  $C_{2-4}$  hydroxyalkyl,  $C_{2-4}$  carboxyalkyl,  $C_{2-4}$  sulfoalkyl or aralkyl group,

- 5  $R^7$  and  $R^8$  independently of one another represent a hydrogen atom, a  $C_{1-4}$  alkyl group, a halogen atom, a hydroxy,  $C_{1-4}$  alkoxy or nitro group or together form a fused aromatic ring,

$R^9$  represents a hydrogen atom, a  $C_{1-4}$  alkyl or an aryl group,

- 10  $X$  is an oxygen or sulfur atom, the group  $>N-R^{12}$  or  $-CH=CH-$ , where  $R^{12}$  is a  $C_{1-4}$  alkyl,  $C_{2-4}$  carboxyalkyl,  $C_{2-4}$  sulfoalkyl,  $C_{2-4}$  sulfoxyalkyl,  $C_{2-4}$  hydroxyalkyl or aralkyl group, and

$Y^-$  is an anion selected from halide,  $C_{1-4}$  alkyl sulfate,  $C_{1-4}$  alkane sulfonate, arene sulfonate,  $C_{1-4}$  perfluoroalkanesulfonate, tetrafluoroborate, perhalogenate, sulfate, hydrogen sulfate or carboxylate,



in which

- 15  $R^{10}$  is a  $C_{1-4}$  acyl group, aroyl,  $C_{1-4}$  alkylsulfonyl,  $C_{1-4}$  alkylsulfinyl,  $C_{1-4}$  alkylamino, di- $C_{1-4}$ -alkylamino, vinylcarbonyl, methineimino, nitrile, ester or carboxylic acid amide group which may optionally be substituted by  $C_{1-4}$
- 20 alkyl,  $C_{2-4}$  hydroxyalkyl or aryl groups and

$R^{11}$  is a  $C_{1-4}$  acyl,  $C_{1-4}$  alkoxy,  $C_{1-4}$  alkylamino,  $C_{1-4}$  acylamino or di- $C_{1-4}$ -alkylamino group,

the substituents  $R^{10}$  and  $R^{11}$  together with the rest of the molecule forming

a 5-, 6- or 7-membered heterocycle from the series of 1,3-thiazolidine-2,5-diones, 1,3-thiazolidine-2-thione-5-ones, perhydropyrimidine-2,4,6-triones, perhydropyrimidine-2-thione-4,6-diones, cyclopentane-1,3-diones, cyclohexane-1,3-diones, indolines, indan-1,3-diones, indan-1-ones, 2-pyrazoline-5-ones, 1,2-dihydro-6-hydroxy-2-hydroxypyridines or enol esters thereof, and

Z represents oxygen, sulfur or the dicyanomethylene group, and/or reaction products of these compounds and typical cosmetic ingredients is applied to the keratin-containing fibers, left thereon for a while, usually about 30 minutes, and then rinsed out or washed out with a shampoo.

The aromatic aldehydes or ketones corresponding to formula I and the CH-active compounds corresponding to formula II and/or III may be applied to the hair either simultaneously or successively; in the latter case, it does not matter which of the two components is applied first. The ammonium or metal salts optionally present may be added to the first component or to the second component. A period of up to 30 minutes may elapse between application of the first component and the second component. The fibers may also be pretreated with the salt solution.

The aromatic aldehydes or ketones corresponding to formula I and the CH-active compounds corresponding to formulae II and/or III may be stored either separately or together either in a liquid or paste-form preparation (water-based or water-free) or as a dry powder. In the event of separate storage, the components are thoroughly mixed together just before application. In the event of dry storage, a certain quantity of warm (30 to 80°C) water is normally added and a homogeneous mixture prepared before application.

### Examples

#### **Preparation of a coloring solution:**

Suspensions of 5 mmol of an aromatic aldehyde or ketone corresponding to formula I and 5 mmol of a CH-active compound corresponding to formula II or III in 25 ml of water at 60°C were prepared. After cooling to 30°C, the suspensions were mixed together, 5 mmol of sodium acetate, optionally 5 mmol of piperidine and one drop of a 20% fatty alkyl ether sulfate solution were added and the pH was adjusted accordingly with dilute NaOH or hydrochloric acid.

Where reaction products of the compounds of formula I and compounds of formula II or III were used, 5 mmol of the reaction product was suspended or dissolved in 50 ml of water.

A tress of 90% grey, non-pretreated human hair was placed in this coloring solution for 30 minutes at 30°C. The tress was then rinsed for 30 seconds with luke-warm water, dried with warm air and then combed out.

The particular shades and depths of color are shown in the following Tables.

The depth of color was evaluated on the following scale:

- |       |   |                                 |
|-------|---|---------------------------------|
| -     | : | very faint, if any, color       |
| (+)   | : | weak intensity                  |
| +     | : | medium intensity                |
| +(+)  | : | medium to strong intensity      |
| ++    | : | strong intensity                |
| ++(+) | : | strong to very strong intensity |
| +++   | : | very strong intensity           |

**Table 1**

<b>Aromatic aldehyde or ketone</b>	<b>Compound of formula II or III</b>	<b>Color intensifier</b>	<b>pH</b>	<b>Color</b>	<b>Intensity</b>
4-Dimethylamino-benzaldehyde	1-Ethyl-2-methyl quinolinium iodide	Piperidine	9.0	Violet-red	++(+)
4-Dimethylamino-benzaldehyde	1,4-Dimethyl quinolinium methane sulfonate	Piperidine	9.0	Red-violet	+(+)
4-Dimethylamino-benzaldehyde	3-Ethyl-2-methylbenzo-thiazolium-p-toluene-sulfonate	Piperidine	7.60	Bright pinky red	+++
4-Dimethylamino-benzaldehyde	Rhodanine	Piperidine	7.60	Bright orange	++(+)
4-Dimethylamino-benzaldehyde	Oxindole	Piperidine	9.00	Gold-yellow	++(+)
4-Dimethylamino-benzaldehyde	1,3-Diethylthiobarbituric acid	--	9.00	Orange	++
4-Dimethylamino-benzaldehyde	1-Ethyl-2-methylnaphtho-[1,2-d]-thiazolium-p-toluenesulfonate	--	6.00	Carmine red	++(+)
4-Dimethylamino-1-naphthaldehyde	1-Ethyl-2-methylnaphtho-[1,2-d]-thiazolium-p-toluenesulfonate	--	6.00	Dark violet	++(+)

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Table 1 continued

Aromatic aldehyde or ketone	Compound of formula II or III	Color intensifier	pH	Color	Intensity
4-Dimethylamino-1-naphthaldehyde	3-Ethyl-2-methylbenzothiazolium-p-toluenesulfonate	Piperidine	7.73	Red violet	++(+)
4-Dimethylamino-1-naphthaldehyde	1-Ethyl-2-methylquinolinium iodide	Piperidine	9.00	Violet-brown	+(+)
4-Dimethylamino-cinnamaldehyde	1-Ethyl-2-methylquinolinium iodide	Piperidine	9.00	Dark orange-brown	++(+)
4-Dimethylamino-cinnamaldehyde	3-Ethyl-2-methylbenzothiazolium-p-toluenesulfonate	Piperidine	7.33	Brown	++
4-Dimethylamino-cinnamaldehyde	Rhodanine	--	6.00	Red-orange	++
4-Dimethylamino-cinnamaldehyde	Rhodanine acetic acid	--	6.00	Orange-red	++(+)
4-Dimethylamino-cinnamaldehyde	1,3-Diethyl thiobarbituric acid	--	9.00	Brown-violet	++
4-Dimethylamino-cinnamaldehyde	1,4-Dimethyl quinolinium methane sulfonate	Piperidine	9.00	Dark yellow-brown	++

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Table 1 continued

Aromatic aldehyde or ketone	Compound of formula II or III	Color intensifier	pH	Color	Intensity
1,3,3-Trimethyl-2-formylmethylene indoline (tribase aldehyde)	1,4-Dimethylquinolinium methanesulfonate	Piperidine	9.00	Grey-green	+
Tribase aldehyde	3-Ethyl-2-methylbenzoxazolium iodide	--	6.00	Pinky red	+
Tribase aldehyde	3-Ethyl-2-methylbenzoxazolium iodide	Piperidine	9.00	Dark pinky red	++(+)
Tribase aldehyde	3-Ethyl-2-methylbenzothiazolium-p-toluenesulfonate	Piperidine	8.50	Pinky red (pink)	++
Tribase aldehyde	3-Ethyl-2-methylnaphtho[1,2-d]-thiazolium-p-toluenesulfonate	--	7.27	Violet-orange	+
1-Methylindole-3-aldehyde	1-Ethyl-2-methylnaphtho[1,2-d]-thiazolium-p-toluenesulfonate	--	6.00	Red-orange	++(+)
Indole-3-aldehyde	1-Ethyl-2-methylnaphtho[1,2-d]-thiazolium-p-toluenesulfonate	--	6.00	Yellow-orange	+
Indole-3-aldehyde	3-Ethyl-2-methylbenzothiazolium iodide	--	6.00	Gold-yellow	+

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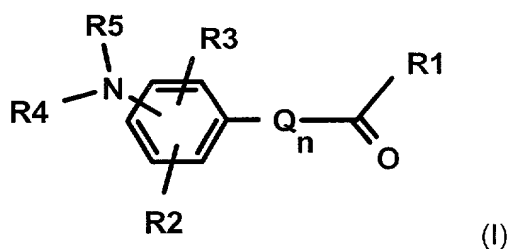
**Table 2**Coloring with reaction products of compounds I and II

Reaction product	Color	Intensity	pH
2-(4-Dimethylaminostyryl)-1-ethylpyridinium iodide	Bright orange	+++	6.00
2-(4-Dimethylaminostyryl)-1-methylquinolinium iodide	Violet-red	++(+)	6.00
4-[(1-methyl-4(1H)-pyridinylidene)-ethylidene-2,5-cyclohexadien-1-one	Orange-yellow	+(+)	6.00
3-(4-Dimethylaminobenzylidene)-2-indolinone	Gold-yellow	++	6.00
5-(4-Dimethylaminobenzylidene)-5-thioxo-2-pyrrolidinone	Bright orange	++	6.00
2-(4-Dimethylaminostyryl)-3-ethylbenzothiazolium iodide	Bright orange	++	6.00

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**CLAIMS**

1. A composition for coloring keratin-containing fibers, more particularly human hair, containing as a coloring component a combination of aromatic aldehydes or ketones corresponding to formula I:



in which

$R^1$  is a hydrogen atom, a  $C_{1-4}$  alkyl or an aryl group,

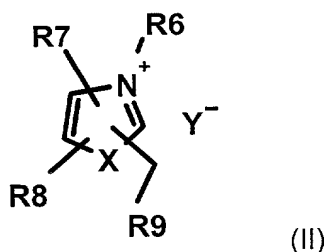
$R^2$  and  $R^3$  independently of one another represent a hydrogen atom, a  $C_{1-4}$  alkyl group, a halogen atom, a hydroxy,  $C_{1-4}$  alkoxy or nitro group or together form a fused aromatic ring,

$R^4$  and  $R^5$  represent a hydrogen atom, a  $C_{1-4}$  alkyl,  $C_{2-4}$  hydroxyalkyl,  $C_{1-4}$  alkenyl or aryl group or, together with the nitrogen atom, form a five- to seven-membered heterocyclic ring or one of them forms a saturated or unsaturated 5-, 6- or 7-membered ring with one of the substituents  $R^2$  or  $R^3$ ,

Q is a direct bond or a vinylene or vinylidene group which, together with one of the two substituents  $R^4$  or  $R^5$ , may form an indole ring or - where an exocyclic double bond is formed - an indoline ring and

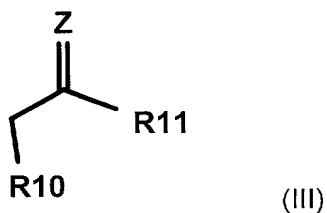
$n = 1$  or  $2$ ,

and CH-active compounds corresponding to formulae II and/or III:



in which

- $R^6$  is a  $C_{1-10}$  alkyl,  $C_{2-10}$  alkenyl,  $C_{2-4}$  hydroxyalkyl,  $C_{2-4}$  carboxyalkyl,  $C_{2-4}$  sulfoalkyl or aralkyl group,
- $R^7$  and  $R^8$  independently of one another represent a hydrogen atom, a  $C_{1-4}$  alkyl group, a halogen atom, a hydroxy,  $C_{1-4}$  alkoxy or nitro group or together form a fused aromatic ring,
- $R^9$  represents a hydrogen atom, a  $C_{1-4}$  alkyl or an aryl group,
- $X$  is an oxygen or sulfur atom, the group  $>N-R^{12}$  or  $-CH=CH-$ , where  $R^{12}$  is a  $C_{1-4}$  alkyl,  $C_{2-4}$  carboxyalkyl,  $C_{2-4}$  sulfoalkyl,  $C_{2-4}$  sulfoxyalkyl,  $C_{2-4}$  hydroxyalkyl or aralkyl group, and
- $Y^-$  is an anion selected from halide,  $C_{1-4}$  alkyl sulfate,  $C_{1-4}$  alkane sulfonate, arene sulfonate,  $C_{1-4}$  perfluoroalkanesulfonate, tetrafluoroborate, perhalogenate, sulfate, hydrogen sulfate or carboxylate,



in which

- $R^{10}$  is a  $C_{1-4}$  acyl group, aroyl,  $C_{1-4}$  alkylsulfonyl,  $C_{1-4}$  alkylsulfinyl,  $C_{1-4}$  alkylamino, di- $C_{1-4}$ -alkylamino, vinylcarbonyl, methineimino, nitrile, ester or carboxylic acid amide group which may optionally be substituted by  $C_{1-4}$  alkyl,  $C_{2-4}$  hydroxyalkyl or aryl groups and
- $R^{11}$  is a  $C_{1-4}$  acyl,  $C_{1-4}$  alkoxy,  $C_{1-4}$  alkylamino,  $C_{1-4}$  acylamino or di- $C_{1-4}$ -alkylamino group,

the substituents R<sup>10</sup> and R<sup>11</sup> together with the rest of the molecule forming a 5-, 6- or 7-membered heterocycle from the series of 1,3-thiazolidine-2,5-diones, 1,3-thiazolidine-2-thione-5-ones, perhydropyrimidine-2,4,6-triones, perhydropyrimidine-2-thione-4,6-diones, cyclopentane-1,3-diones, cyclohexane-1,3-diones, indoles, indan-1,3-diones, indan-1-ones, 2-pyrazoline-5-ones, 1,2-dihydro-6-hydroxy-2-hydroxypyridines or enol esters thereof, and

Z represents oxygen, sulfur or the dicyanomethylene group, and/or reaction products of these compounds.

2. A composition as claimed in claim 1, characterized in that 4-dimethylaminobenzaldehyde, 4-diethylaminobenzaldehyde, 4-dimethylamino-2-hydroxybenzaldehyde, 4-pyrrolidinobenzaldehyde, 4-morpholinobenzaldehyde, 4-piperidinobenzaldehyde, 4-dimethylaminoacetophenone, 4-dimethylaminonaphthaldehyde, 4-dimethylaminobenzylidene acetone, 4-dimethylamino cinnamaldehyde, 2-dimethylaminobenzaldehyde, 2-chloro-4-dimethylaminobenzaldehyde, 4-dimethylamino-2-methylbenzaldehyde, trans-4-diethylaminocinnamaldehyde, 4-(dibutylamino)-benzaldehyde, 4-diphenylaminobenzaldehyde, 2,3,6,7-tetrahydro-1H,5H-benzo[ij]quinoxiline-9-carboxaldehyde, 4-dimethylamino-2-methoxybenzaldehyde, 2,3,6,7-tetrahydro-8-hydroxy-1H,5H-benzo[ij]quinoxiline-9-carboxaldehyde, 4-(1-imidazolyl)-benzaldehyde, 2-morpholinobenzaldehyde, indole-3-carboxaldehyde, 1-methylindole-3-carboxaldehyde, N-ethylcarbazole-3-aldehyde, 2-formylmethylene-1,3,3-trimethylindoline (Fischer's aldehyde or tribase aldehyde) and mixtures thereof are used as the compounds of formula I.

3. A composition as claimed in claim 1 or 2, characterized in that 1,4-dimethylquinolinium, 1,2-dimethylquinolinium, 1,4-dimethylpyridinium, 1,2-dimethylpyridinium, 2-methyl-1-ethylquinolinium, 2,3-dimethylisoquinolinium, 1,2,3,3-tetramethyl-3H-indolinium, 2,3-dimethylbenzothiazolium, 2,3-dimethyl-6-nitrobenzothiazolium, 3-benzyl-2-benzothiazolium, 2-methyl-3-

propyl benzothiazolium, 2,4-dimethyl-3-ethylthiazolium, 3-(2-carboxyethyl)-2,5-dimethylbenzothiazolium, 1,2,3-trimethylbenzimidazolium, 5,6-dichloro-1,3-diethyl-2-methyl benzimidazolium, 3-ethyl-2-methylbenzothiazolium, 3-ethyl-2-methylnaphtho[1,2-d]thiazolium, 5-chloro-3-ethyl-2-methylbenzothiazolium, 3-ethyl-2-methyl benzoxazolium salts which may be present, for example, as chlorides, bromides, iodides, methanesulfonates, benzenesulfonates, p-toluenesulfonates, trifluoromethane sulfonates, methyl sulfates, tetrafluoroborates and 2-methyl-3-(3-sulfopropyl)-benzothiazolium hydroxide, inner salt, 5-methoxy-2-methyl-3-(3-sulfopropyl)-benzothiazolium hydroxide, inner salt and mixtures of the above are used as the compounds of formula II.

4. A composition as claimed in any of claims 1 to 3, characterized in that rhodanine, rhodanine-3-acetic acid, barbituric acid, thiobarbituric acid, 1,3-dimethyl and 1,3-diethyl thiobarbituric acid, oxindole, 3-indoxyl acetate, coumaranone, 1-methyl-3-phenylpyrazolinone, indan-1,3-dione, cyclopentane-1,3-dione, 1,2-dihydro-1-ethyl-6-hydroxy-4-methyl-2-oxo-3-pyridinecarbonitrile and mixtures of the above are used as the compounds of formula III.

5. A composition as claimed in any of claims 1 to 4, characterized in that the reaction products of the compounds corresponding to formulae I and II and/or III are selected from Quinaldine Red (2-[4-(dimethylamino)-styryl]-1-ethyl quinolinium iodide), 2-[4-(dimethylamino)-styryl]-1-methyl quinolinium iodide, 2-[4-(dimethylamino)-styryl]-1-ethylpyridinium iodide, 2-[4-(dimethylamino)-styryl]-1-methylpyridinium iodide, 4-[4-(dimethylamino)-styryl]-1-methyl pyridinium tosylate, 4-[2-(2,3,6,7-tetrahydro-1H,5H-benzo[*ij*]quinolizin-9-yl)-ethenyl]-1-methylpyridinium iodide, trans-4-[4-(dibutylamino)-styryl]-1-methyl pyridinium iodide and 2,6-bis-[4-(dimethylamino)-styryl]-1-methylpyridinium iodide, 2-[4-(dimethylamino)-styryl]-3-methyl benzoxazolium perchlorate, 2-[4-(dimethylamino)-styryl]-3-methyl benzoxazolium iodide, 2-[4-(dimethylamino)-styryl]-1-

ethylnaphthol[1,2-d]thiazolium iodide and mixtures of the above.

6. A composition as claimed in any of claims 1 to 5, characterized in that the aromatic aldehydes or ketones corresponding to formula I and the quaternary heterocyclic compounds corresponding to formula II and the CH-active compounds corresponding to formula III are used in quantities of 0.03 to 65 mmol and more particularly 1 to 40 mmol, based on 100 g of the colorant as a whole.

7. A composition as claimed in any of claims 1 to 6, characterized in that it contains color intensifiers selected from the group consisting of piperidine, piperidine-2-carboxylic acid, piperidine-3-carboxylic acid, piperidine-4-carboxylic acid, pyridine, 2-hydroxypyridine, 3-hydroxypyridine, 4-hydroxypyridine, imidazole, 1-methyl imidazole, histidine, pyrrolidine, proline, pyrrolidone, pyrrolidone-5-carboxylic acid, pyrazole, 1,2,4-triazole, piperazine or mixtures thereof.

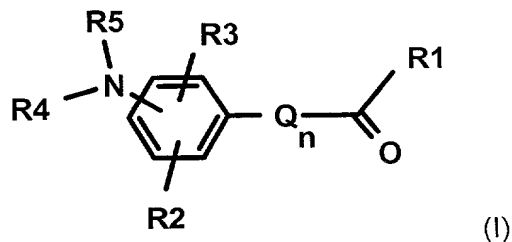
8. A composition as claimed in any of claims 1 to 7, characterized in that it contains substantive dyes from the group of nitrophenylenediamines, nitroaminopenols, anthraquinones or indophenols, preferably in a quantity of 0.01 to 20% by weight, based on the colorant as a whole.

9. A composition as claimed in any of claims 1 to 8, characterized in that ammonium or metal salts selected from the group of formates, carbonates, halides, sulfates, butyrates, valerates, caproates, acetates, lactates, glycolates, tartrates, citrates, gluconates, propionates, phosphates and phosphonates of alkali metals, such as potassium, sodium or lithium, alkaline earth metals, such as magnesium, calcium, strontium or barium, or of aluminium, manganese, iron, cobalt, copper or zinc are added.

10. A composition as claimed in any of claims 1 to 9, characterized in that it contains oxidizing agents, more particularly  $H_2O_2$ , in a quantity of 0.01 to 6% by weight, based on the solution applied.

11. A composition as claimed in any of claims 1 to 10, characterized in that it contains anionic, zwitterionic or nonionic surfactants.

12. The use of a combination of aromatic aldehydes or ketones corresponding to formula I:



5

in which

$R^1$  is a hydrogen atom, a  $C_{1-4}$  alkyl or an aryl group,

$R^2$  and  $R^3$  independently of one another represent a hydrogen atom, a  $C_{1-4}$  alkyl group, a halogen atom, a hydroxy,  $C_{1-4}$  alkoxy or nitro group or

10 together form a fused aromatic ring,

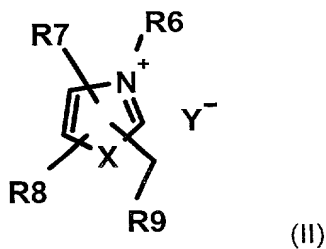
$R^4$  and  $R^5$  represent a hydrogen atom, a  $C_{1-4}$  alkyl,  $C_{2-4}$  hydroxyalkyl,  $C_{1-4}$  alkenyl or aryl group or, together with the nitrogen atom, form a five- to seven-membered heterocyclic ring or one of them forms a saturated or unsaturated 5-, 6- or 7-membered ring with one of the substituents  $R^2$  or

15  $R^3$ ,

$Q$  is a direct bond or a vinylene or vinylidene group which, together with one of the two substituents  $R^4$  or  $R^5$ , may form an indole ring or - where an exocyclic double bond is formed - an indoline ring and

$n = 1$  or  $2$ ,

20 and CH-active compounds corresponding to formulae II and/or III:





in which

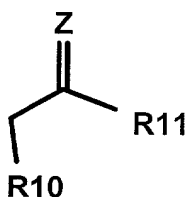
$R^6$  is a  $C_{1-10}$  alkyl,  $C_{2-10}$  alkenyl,  $C_{2-4}$  hydroxyalkyl,  $C_{2-4}$  carboxyalkyl,  $C_{2-4}$  sulfoalkyl or aralkyl group,

- 5  $R^7$  and  $R^8$  independently of one another represent a hydrogen atom, a  $C_{1-4}$  alkyl group, a halogen atom, a hydroxy,  $C_{1-4}$  alkoxy or nitro group or together form a fused aromatic ring,

$R^9$  represents a hydrogen atom, a  $C_{1-4}$  alkyl or an aryl group,

- 10 X is an oxygen or sulfur atom, the group  $>N-R^{12}$  or  $-CH=CH-$ , where  $R^{12}$  is a  $C_{1-4}$  alkyl,  $C_{2-4}$  carboxyalkyl,  $C_{2-4}$  sulfoalkyl,  $C_{2-4}$  sulfoxyalkyl,  $C_{2-4}$  hydroxyalkyl or aralkyl group, and

$Y^-$  is an anion selected from halide,  $C_{1-4}$  alkyl sulfate,  $C_{1-4}$  alkane sulfonate, arene sulfonate,  $C_{1-4}$  perfluoroalkanesulfonate, tetrafluoroborate, perhalogenate, sulfate, hydrogen sulfate or carboxylate,



(III)

in which

$R^{10}$  is a  $C_{1-4}$  acyl group, aroyl,  $C_{1-4}$  alkylsulfonyl,  $C_{1-4}$  alkylsulfinyl,  $C_{1-4}$  alkylamino, di- $C_{1-4}$ -alkylamino, vinylcarbonyl, methineimino, nitrile, ester or carboxylic acid amide group which may optionally be substituted by  $C_{1-4}$

- 20 alkyl,  $C_{2-4}$  hydroxyalkyl or aryl groups and

$R^{11}$  is a  $C_{1-4}$  acyl,  $C_{1-4}$  alkoxy,  $C_{1-4}$  alkylamino,  $C_{1-4}$  acylamino or di- $C_{1-4}$ -alkylamino group,

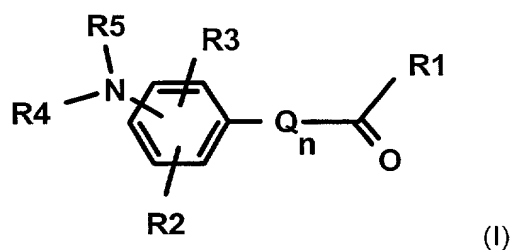
- the substituents  $R^{10}$  and  $R^{11}$  together with the rest of the molecule forming a 5-, 6- or 7-membered heterocycle from the series of 1,3-thiazolidine-2,5-diones, 1,3-thiazolidine-2-thione-5-ones, perhydropyrimidine-2,4,6-triones, perhydropyrimidine-2-thione-4,6-diones, cyclopentane-1,3-diones, cyclohexane-1,3-diones, indolines, indan-1,3-diones, indan-1-ones, 2-
- 25

pyrazoline-5-ones, 1,2-dihydro-6-hydroxy-2-hydroxypyridines or enol esters thereof, and

Z represents oxygen, sulfur or the dicyanomethylene group, and/or reaction products of these compounds,

5 as a coloring component in oxidation hair colorants.

13. A process for coloring keratin-containing fibers, more particularly human hair, in which a colorant containing a combination of aromatic aldehyde or ketones corresponding to formula I:



in which

R<sup>1</sup> is a hydrogen atom, a C<sub>1-4</sub> alkyl or an aryl group,

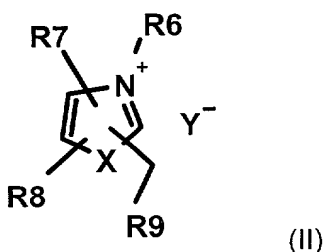
15 R<sup>2</sup> and R<sup>3</sup> independently of one another represent a hydrogen atom, a C<sub>1-4</sub> alkyl group, a halogen atom, a hydroxy, C<sub>1-4</sub> alkoxy or nitro group or together form a fused aromatic ring,

R<sup>4</sup> and R<sup>5</sup> represent a hydrogen atom, a C<sub>1-4</sub> alkyl, C<sub>2-4</sub> hydroxyalkyl, C<sub>1-4</sub> alkenyl or aryl group or, together with the nitrogen atom, form a five- to seven-membered heterocyclic ring or one of them forms a saturated or  
 20 unsaturated 5-, 6- or 7-membered ring with one of the substituents R<sup>2</sup> or R<sup>3</sup>,

Q is a direct bond or a vinylenic or vinylidene group which, together with one of the two substituents R<sup>4</sup> or R<sup>5</sup>, may form an indole ring or - where an exocyclic double bond is formed - an indoline ring and

25 n = 1 or 2,

and CH-active compounds corresponding to formulae II and/or III:



in which

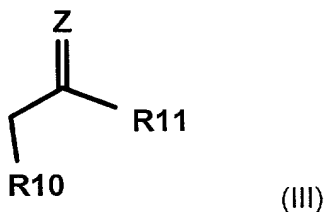
$R^6$  is a  $C_{1-10}$  alkyl,  $C_{2-10}$  alkenyl,  $C_{2-4}$  hydroxyalkyl,  $C_{2-4}$  carboxyalkyl,  $C_{2-4}$  sulfoalkyl or aralkyl group,

- 5  $R^7$  and  $R^8$  independently of one another represent a hydrogen atom, a  $C_{1-4}$  alkyl group, a halogen atom, a hydroxy,  $C_{1-4}$  alkoxy or nitro group or together form a fused aromatic ring,

$R^9$  represents a hydrogen atom, a  $C_{1-4}$  alkyl or an aryl group,

- 10  $X$  is an oxygen or sulfur atom, the group  $>N-R^{12}$  or  $-CH=CH-$ , where  $R^{12}$  is a  $C_{1-4}$  alkyl,  $C_{2-4}$  carboxyalkyl,  $C_{2-4}$  sulfoalkyl,  $C_{2-4}$  sulfoxyalkyl,  $C_{2-4}$  hydroxyalkyl or aralkyl group, and

$Y^-$  is an anion selected from halide,  $C_{1-4}$  alkyl sulfate,  $C_{1-4}$  alkane sulfonate, arene sulfonate,  $C_{1-4}$  perfluoroalkanesulfonate, tetrafluoroborate, perhalogenate, sulfate, hydrogen sulfate or carboxylate,



in which

$R^{10}$  is a  $C_{1-4}$  acyl group, aroyl,  $C_{1-4}$  alkylsulfonyl,  $C_{1-4}$  alkylsulfinyl,  $C_{1-4}$  alkylamino, di- $C_{1-4}$ -alkylamino, vinylcarbonyl, methineimino, nitrile, ester or carboxylic acid amide group which may optionally be substituted by  $C_{1-4}$

- 20 alkyl,  $C_{2-4}$  hydroxyalkyl or aryl groups and

$R^{11}$  is a  $C_{1-4}$  acyl,  $C_{1-4}$  alkoxy,  $C_{1-4}$  alkylamino,  $C_{1-4}$  acylamino or di- $C_{1-4}$ -alkylamino group,

the substituents  $R^{10}$  and  $R^{11}$  together with the rest of the molecule forming

a 5-, 6- or 7-membered heterocycle from the series of 1,3-thiazolidine-2,5-diones, 1,3-thiazolidine-2-thione-5-ones, perhydropyrimidine-2,4,6-triones, perhydropyrimidine-2-thione-4,6-diones, cyclopentane-1,3-diones, cyclohexane-1,3-diones, indolines, indan-1,3-diones, indan-1-ones, 2-pyrazoline-5-ones, 1,2-dihydro-6-hydroxy-2-hydroxypyridines or enol esters thereof, and

Z represents oxygen, sulfur or the dicyanomethylene group, and/or reaction products of these compounds and typical cosmetic ingredients is applied to the keratin-containing fibers, left thereon for a while, usually about 30 minutes, and then rinsed out or washed out with a shampoo.

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(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES  
PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

(19) Weltorganisation für geistiges Eigentum  
Internationales Büro



(43) Internationales Veröffentlichungsdatum  
1. März 2001 (01.03.2001)

PCT

(10) Internationale Veröffentlichungsnummer  
**WO 01/13866 A1**

(51) Internationale Patentklassifikation<sup>7</sup>: **A61K 7/13**

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(21) Internationales Aktenzeichen: PCT/EP00/07163

(22) Internationales Anmeldedatum:  
2. August 2000 (02.08.2000)

(81) Bestimmungsstaaten (*national*): AU, JP, US.

(25) Einreichungssprache: Deutsch

(84) Bestimmungsstaaten (*regional*): europäisches Patent (AT,  
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(30) Angaben zur Priorität:  
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**Veröffentlicht:**

- Mit internationalem Recherchenbericht.
- Vor Ablauf der für Änderungen der Ansprüche geltenden Frist; Veröffentlichung wird wiederholt, falls Änderungen eintreffen.

(71) Anmelder (für alle Bestimmungsstaaten mit Ausnahme von US): **HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN** [DE/DE]; Henkelstr. 67, 40589 Düsseldorf (DE).

Zur Erklärung der Zweibuchstaben-Codes, und der anderen Abkürzungen wird auf die Erklärungen ("Guidance Notes on Codes and Abbreviations") am Anfang jeder regulären Ausgabe der PCT-Gazette verwiesen.

(72) Erfinder; und

(75) Erfinder/Anmelder (nur für US): **MÖLLER, Hinrich** [DE/DE]; Haydnstr. 27, 40789 Monheim (DE).

(54) Title: AGENT FOR DYING KERATIN FIBERS

(54) Bezeichnung: MITTEL ZUM FÄRBen VON KERATINHALTIGEN FASERN

(57) Abstract: The invention relates to an agent for dyeing keratin fibers, especially human hair. Said agent contains at least one combination comprised of aromatic aldehydes or ketones and of CH-active compounds.

(57) Zusammenfassung: Es wird ein Mittel zum Färben von keratinhaltigen Fasern, insbesondere menschlichen Haaren, beansprucht, enthaltend mindestens eine Kombination aus aromatischen Aldehyden bzw. Ketonen und CH-aktiven Verbindungen.

WO 01/13866 A1

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PTO/SB/01 (6-95)

Approved for use through: 10/31/98 OMB 0651-0032

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<p>0010/PTO Rev. 6/95</p> <p style="text-align: center;"><b>DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION</b></p> <p><input type="checkbox"/> Declaration Submitted with Initial Filing    OR    <input checked="" type="checkbox"/> Declaration Submitted after Initial Filing</p>	<table border="1" style="width: 100%; border-collapse: collapse;"><tr><td style="width: 50%;">Attorney Docket Number</td><td style="width: 50%;">H 4020 PCT/US</td></tr><tr><td>First Named Inventor</td><td>Moeller, Hinrich</td></tr><tr><td colspan="2" style="text-align: center;"><i>COMPLETE IF KNOWN</i></td></tr><tr><td>Application Number</td><td>10/048,208</td></tr><tr><td>Filing Date</td><td></td></tr><tr><td>Group Art Unit</td><td></td></tr><tr><td>Examiner Name</td><td></td></tr></table>	Attorney Docket Number	H 4020 PCT/US	First Named Inventor	Moeller, Hinrich	<i>COMPLETE IF KNOWN</i>		Application Number	10/048,208	Filing Date		Group Art Unit		Examiner Name	
Attorney Docket Number	H 4020 PCT/US														
First Named Inventor	Moeller, Hinrich														
<i>COMPLETE IF KNOWN</i>															
Application Number	10/048,208														
Filing Date															
Group Art Unit															
Examiner Name															

As a below named inventor, I hereby declare that.  
My residence, post office address, and citizenship are as stated below next to my name.  
I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

**AGENT FOR DYING KERATIN FIBERS**

*(Title of the Invention)*

the specification of which

☐ is attached hereto

OR

☒ was filed on (MM/DD/YYYY) 08/02/2000 as United States Application Number or PCT International

Application Number PCT/EP00/07163 and was amended on (MM/DD/YYYY)  (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations, § 1.56

I hereby claim foreign priority benefits under Title 35, United States Code §119(a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT International application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Certified Copy Attached?	
				YES	NO
19936911.9	Germany	08/05/1999	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
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			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

☐ Additional foreign application numbers are listed on a supplemental priority sheet attached hereto:

I hereby claim the benefit under Title 35, United States Code §119(e) of any United States provisional application(s) listed below.

Application Number(s)	Filing Date (MM/DD/YYYY)	<input type="checkbox"/> Additional provisional application numbers are listed on a supplemental priority sheet attached hereto.

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H 4020 PCT/US

## DECLARATION

Page 2

I hereby claim the benefit under Title 35, United States Code §120 of any United States application(s), or §365© of any PCT international application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT international application in the manner provided by the first paragraph of Title 35, United States Code §112.1 acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

U.S. Parent Application Number	PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number (if applicable)
	PCT/EP00/07163	08/02/2000	

☐ Additional U.S. or PCT international application numbers are listed on a supplemental priority sheet attached hereto.

As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

☐ Firm Name  Customer Number  or label

☒ List Attorney(s) and/or agent(s) name and registration number below:

Name	Registration Number	Name	Registration Number
Glenn E. J. Murphy	33,539		
Stephen D. Harper	33,243		
Kimberly R. Hild	39,224		
Steven C. Bauman	33,832		

☐ Additional attorney(s) and/or agent(s) named on a supplemental sheet attached hereto.

Please direct all correspondence to: ☒ Customer Number ☐ or label 00423 OR ☐ Fill in correspondence address below

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Address	Henkel Corporation				
Address	2500 Renaissance Blvd, Suite 200				
City	Gulph Mills	State	PA	Zip	19406
Country	USA	Telephone	610-278-4964	Fax	610-278-6548

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Name of Sole or First Inventor:		<input type="checkbox"/> A petition has been filed for this unsigned inventor					
Given Name	<u>Hinrich</u>	Middle Initial		Family Name	<u>Moeller</u>	Suffix e.g. Jr.	
Inventor's Signature	<u>Hinrich Moeller</u>				Date	<u>9.04.02</u>	
Residence: City	<u>Monheim</u>	State		Country	<u>Germany</u>	Citizenship	<u>Germany</u>
Post Office Address	<u>Haydnstrasse 27</u>						
Post Office Address							
City	<u>40789 Monheim</u>	State		Zip		Country	<u>Germany</u>
						Applicant Authority	

☒ Additional inventors are being named on supplemental sheet(s) attached hereto

(+) inside this box →

H 4020 PCT/US

DECLARATION										ADDITIONAL INVENTOR(S) Supplemental Sheet			
Name of Additional Joint Inventor, if any:										<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name <u>Doris</u>			Middle Initial		Family Name <u>Oberkobusch</u>			Suffix e.g. Jr.					
Inventor's Signature <u>Doris Oberkobusch</u>						Date <u>6.3.02</u>							
Residence: City <u>Duesseldorf</u>			State		Country <u>Germany</u>			Citizenship <u>Germany</u>		DEX			
Post Office Address <u>Auf'm Rott 81</u>													
Post Office Address													
City <u>40591 Duesseldorf</u>			State		Zip		Country <u>Germany</u>		Applicant Authority				
Name of Additional Joint Inventor, if any:										<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name <u>Horst</u>			Middle Initial		Family Name <u>Hoeffkes</u>			Suffix e.g. Jr.					
Inventor's Signature <u>Horst Hoeffkes</u>						Date <u>20.3.02</u>							
Residence: City <u>Duesseldorf</u>			State		Country <u>Germany</u>			Citizenship <u>Germany</u>		DEX			
Post Office Address <u>Carlo-Schmidt-Strasse 113</u>													
Post Office Address													
City <u>40595 Duesseldorf</u>			State		Zip		Country <u>Germany</u>		Applicant Authority				
Name of Additional Joint Inventor, if any:										<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name			Middle Initial		Family Name			Suffix e.g. Jr.					
Inventor's Signature						Date							
Residence: City			State		Country			Citizenship					
Post Office Address													
Post Office Address													
City			State		Zip		Country		Applicant Authority				
Name of Additional Joint Inventor, if any:										<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name			Middle Initial		Family Name			Suffix e.g. Jr.					
Inventor's Signature						Date							
Residence: City			State		Country			Citizenship					
Post Office Address													
Post Office Address													
City			State		Zip		Country		Applicant Authority				
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Given Name			Middle Initial		Family Name			Suffix e.g. Jr.					
Inventor's Signature						Date							
Residence: City			State		Country			Citizenship					
Post Office Address													
Post Office Address													
City			State		Zip		Country		Applicant Authority				
<input type="checkbox"/> Additional inventors are being named on supplemental sheet(s) attached hereto													

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